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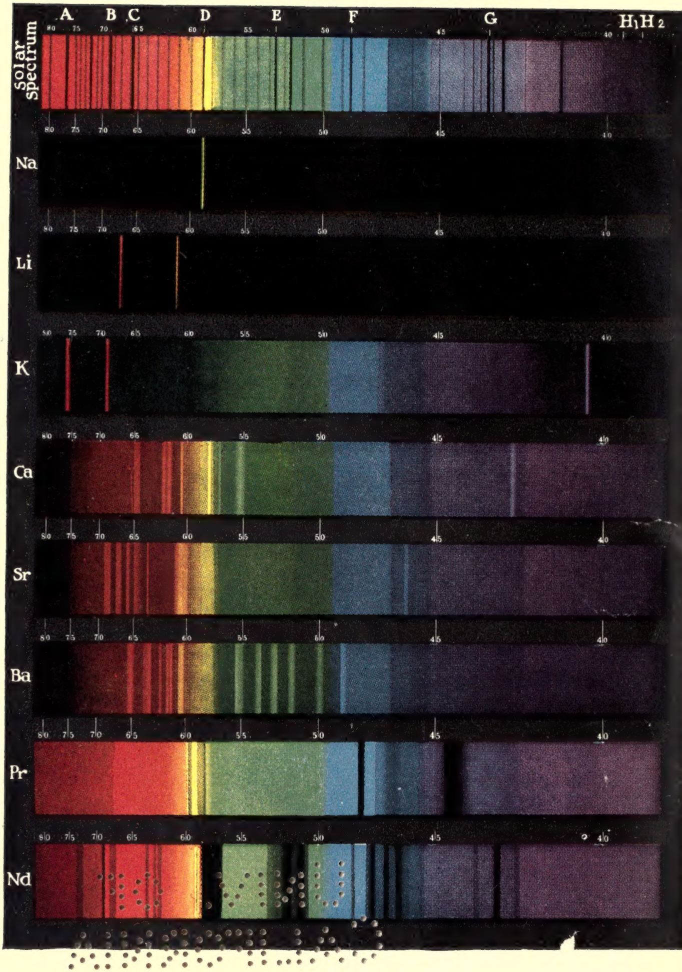

VARIOUS SPECTRA

FIRST PRINCIPLES

OF

CHEMISTRY

BY

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FROM THE PREFACE TO THE FIRST EDITION

In selecting their material for this book, the authors have been governed wholly by what they considered of intrinsic value to the elementary student, without reference to its traditional place in a text-book. This has led to the omission of some subjects commonly found in books for beginners. To the subjects selected they have striven to give a discussion simple enough to be readily comprehended by the beginner, and complete enough to furnish him with a clear idea of the underlying principles of Chemistry and a definite knowledge of its more important facts.

The experimental determination of chemical facts is, then, emphasized from the first. When sufficient facts have been given to make explanation necessary, the generalizations of the science have been introduced. In some of the theoretical chapters, particularly those on solution and ionization, it may be advisable to omit certain portions at first and to take them up afterwards as need arises.

The authors have attempted to bring out the fundamental principles first by a simple statement, which is later developed and driven home by illustrations, exercises, and problems, all designed to stimulate the pupil to think for himself, and constantly to connect his new facts with the facts and principles already learned.

In order to give the pupil some idea of the great commercial importance of Chemistry, a number of typical manufacturing

processes have been described and illustrated. Where a substance is manufactured in several ways, the authors have tried to avoid confusion by giving a description of one process only, selecting the one which they believe is, or will become, most extensively used in this country. The commercial production of copper, aluminum, iron, and carborundum has been described somewhat in detail, for these are notable examples of modern chemical processes.

New York, August, 1907.

PREFACE TO REVISED EDITION

In the preparation of the Revised Edition, an attempt has been made to rid the text of all material that has become obsolete, or that has proved unadapted to a first course in Chemistry. The general spirit and the method of the book, however, have been kept unchanged. Many paragraphs have been recast, in order to make every statement as lucid as possible. A chapter on chemical equilibrium and one on radioactivity have been added; the one on the ground that it represents a principle that is fundamental in the science, the other because of the unusual interest that attaches to the subject.

Among other changes that will be noted in the book are the extension of the treatments of nomenclature and chemical calculations, the addition of a description of the lead chamber process for sulphuric acid, an increase in the number of illustrations, and the substitution of many new cuts for the old. As in the first edition, much attention has been paid to manufacturing processes, in accordance with the authors' beliefs that many chemical principles are best learned through their practical applications, and that a student should get a very large amount of practical information in his first course in chemistry. New processes have been introduced, and former descriptions have been modified to agree with present practice.

The thanks of the authors are gratefully given to all those who have generously assisted them in securing descriptions and illustrations of chemical processes as they are actually

carried on. Mr. Allen B. Doggett has rendered great assistance in photographic work. We are especially indebted to Professor Charles F. Chandler, of Columbia University; to Mr. C. D. McArthur; to Professor L. H. Merrill, of the University of Maine; to Professor Herbert R. Moody, of the College of the City of New York; to Professor Harmon N. Morse, of Johns Hopkins University; to the American Smelting and Refining Company, L. M. Booth Company, Brooklyn Union Gas Company, the Carborundum Company, the Crucible Steel Company of America, National Lead Company, Standard Oil Company, United Sulphur Company, and to the *Scientific American*, for assistance which they have rendered.

NEW YORK, June, 1915.

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PORTRAITS OF DISTINGUISHED CHEMISTS

FIRST PRINCIPLES OF CHEMISTRY

CHAPTER I

INTRODUCTION

1. Physical Change. — When we notice the things about us, we see that they undergo changes: a piece of wood bends under a weight, or warps when wet; a rod lengthens when heated; a piece of iron placed near a magnet attracts another piece of iron. If we remove the weight from the stick, it straightens; the iron removed from the magnet loses its power of attraction. In such changes, although the object may be considerably altered, we still recognize the pieces of the stick as wood, as we do the fragments of a broken tumbler as glass; that is, the *material* has not lost or changed those peculiar properties or the characteristics by which we identify it. Such changes are called *physical changes;* they result usually in a change of such properties as size, shape, or color.

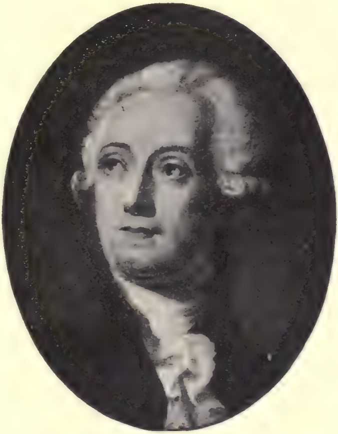
2. Chemical Change. — Another kind of change is seen in the burning of wood. Iron in rusting falls to a red powder; mortar and cement change from a plastic to a stonelike condition; fruits and vegetables decay; meat spoils; milk sours; fruit juices ferment. In all these changes the materials have apparently lost their identity, and substances with new characteristics are formed. We do not find any resemblance between iron and rust or between wood and what remains after it is burned. The iron and the wood have apparently disappeared or changed and we

have new substances in their places. Such alterations are called *chemical changes*. Chemistry is the name given to the science which has grown out of the study of chemical changes and the effort to control or modify them.

The most striking chemical change that goes on about us is that which occurs when a substance burns. If the burning substance is coal or wood, it seems to disappear except for a small quantity of ashes. In studying this change, several questions suggest themselves. What has happened to produce the heat that is given off? What has become of the great mass of substance that has apparently disappeared? Why does the substance burn more brightly when air is blown on it? Why does it stop burning when the air is shut off, as in smothering a flame? If we find answers to these questions, we shall have explained the phenomena of burning.

Early investigators did not discover the true nature of this process. They adopted a wrong explanation, and, as a result, the science of chemistry did not advance. A true explanation was stated only a little more than a hundred years ago. Since that time chemistry has progressed at an astonishing rate. The true explanation of burning was found by studying the change that many metals undergo when heated in air.

3. Heating Metals in Air. — A few metals — for example, magnesium — burn when heated in the air. Most metals undergo a similar, but much slower, change, without the production of light. If a piece of bright copper is heated, it assumes a black color; on bending or scraping it gently, a black powder separates from it. If the metal is heated again, another layer of the black substance forms. By repeating the process a sufficient number of times, the piece of copper can be entirely changed into the black powder.



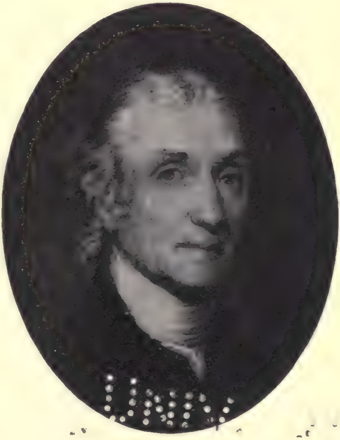
Antoine Laurent Lavoisier (1743–1794) was a French investigator and scientific interpreter. When twenty-five, he was chosen adjunct member of the French Academy, and became one of the leading scientists of his time.

Lavoisier studied combustion and showed by quantitative experiments that the weight of the product exceeds the weight of the fuel. He explained the composition of air and of water and advanced the doctrine of indestructibility of matter.

Joseph Priestley (1733-1804) was an English writer on religion, politics, and science. He was a brilliant investigator and experimenter. His experiments suggested to him that plants and animals produce opposite changes in the air.

Priestley discovered several gases, notably oxygen. This he prepared by heating mercury oxide.

The latter years of Priestley's life were passed in Pennsylvania.



Since the black powder in no way resembles the copper from which it was prepared, a chemical change has taken place. Iron heated in a similar manner gives a somewhat similar result. Lead after melting gives a yellowish powder; zinc, if in the form of a powder, will take fire and yield a white powder. Metals, in general, when thus heated produce powdered substances which bear little or no resemblance to the original metal. In some cases the change is very slow and often difficult to bring about, unless the metal is in small pieces or powdered and the heating carefully regulated. Gold and platinum show no change on heating in the air.

Several things may be thought of as explanations of the change which the metals first described undergo. It may be that by the effect of the heat, without the aid of any substance, the metal is transformed into a new kind of matter; possibly the metal in being heated has lost some of its substance, which has passed off as gas; possibly the metal has absorbed something from the air.

As an aid in testing these possible explanations, it will be advisable to weigh the metal before and after it is heated. When this is done, it will be found that *the powder always weighs more than the metal* from which it was formed. This seems to indicate that during the heating the metal adds to itself more substance, and that this substance is taken from the air. To further test this conclusion, a piece of metal can be sealed in a glass tube from which the air has been exhausted; *heated under these conditions, the metal is not changed.*

4. Lavoisier's Experiment. — Another conclusive experiment showing the change of metals on being heated in the air is one that was performed by Lavoisier, the French chemist, to whom is given the credit of discovering the

nature of this kind of chemical change. He put some tin in a good-sized glass flask and sealed it so that the air could neither enter nor leave it. He then heated the flask carefully for several days. At the end of this time, he noticed that a certain amount of white powder had been formed. He next ascertained that the flask with its contents had not changed in weight. He then opened the neck of the flask and noticed that air rushed in. On again weighing the flask and its contents, he found that there was an increase in weight, and that this increase was equal to the increase which the tin had undergone on being converted into the white powder. He explained these facts as follows: the tin on being heated combined with some of the air in the flask, producing the white powder. The flask as a whole did not increase in weight because no air entered the flask to take the place of that which had combined with the tin. When the flask was opened, the air entered, causing the increase in weight.

Since experience has shown that matter can be neither created nor destroyed, it appears probable that the powdered substances are more complex than the metals from which they are formed; that is, they contain the metal plus something which has been taken from the air. Lavoisier undertook to find out the nature of the substance which was taken from the air.

5. Heating Mercury in the Air.—Mercury, heated in the air, underwent a much less rapid change than the metals of which we have been speaking. Kept at a temperature a little below its boiling point for several days a small quantity of red powder was gradually formed (Fig. 1). A quantity of this powder was heated in a glass tube to a temperature above the boiling point of mercury, and a colorless gas was given off.

A glowing splinter was inserted into the tube. It burst into flame and burned brilliantly. The gas could not have been ordinary air, for a splinter does not behave so in air. A quantity of the gas was collected and was shown to be very different from ordinary air by the fact that substances burned in it with extraordinary vigor.

On examining the tube it was found that a part or all

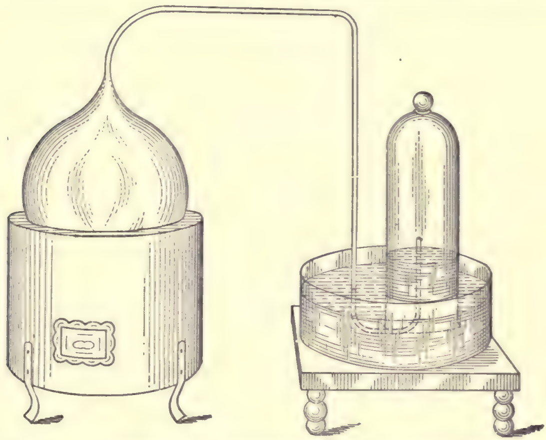


FIG. 1. — LAVOISIER'S APPARATUS FOR HEATING MERCURY.

of the red powder had disappeared and that drops of mercury had collected on the sides of the tube. It appears from this experiment that *the red powder had decomposed into mercury and a gas* which readily supports combustion. Lavoisier named this gas *oxygen.*

Since the red powder was made by heating mercury in the air, and was not formed unless air was present, *the oxygen must have come from the air.* Hence air must contain oxygen. That air is not all oxygen is shown by the fact that only about one fifth, and not all, of the air was absorbed in Lavoisier's experiments; and also by the fact that substances do not burn as readily in air as in oxygen.

The powders obtained by burning tin or copper or iron weigh more than the original piece of metal, because the metal has combined with a noticeable weight of oxygen from the air. In these cases, it is not practical to separate the metal from the oxygen by heat alone.

6. Burning. — The burning of wood or other substances is a process that closely resembles the change of a metal into a compound of the metal and oxygen. In the case of ordinary combustible materials, the products are chiefly gases which pass off unseen. By the use of suitable apparatus, the products formed in the burning of a candle can be collected, and it is found that their weight is greater than the weight of the candle burned. As in the case of the metals, this increase in weight is due to the oxygen taken up from the air. If air is excluded, the burning substance is extinguished, because it can no longer combine with oxygen.

7. Compounds and Elements. — We have shown that the red substance contains oxygen and mercury. The substance formed on heating copper in the air contains oxygen and copper. As these substances formed are composed of more than one kind of material, they are called *compounds*. A compound is a substance that can be separated into two or more substances. No one has changed copper or mercury into anything else, without *adding something*. So far as we know, gold, iron, oxygen, and about eighty other things are not composed of anything else. They are simple substances, or, as we say, *elements*. An element is a substance that has not been separated into other substances by man. A list of elements is given in Table I, Appendix.

8. Solids, Liquids, and Gases. — We have spoken of metals, powders, air, and oxygen as things that may be

weighed. They are forms of *matter*. Matter is generally defined as anything that occupies space. The different kinds of matter are called *substances*. Substances differ in the way they fill space, and it is this difference that determines their *physical state*. The three physical states of matter are the solid, the liquid, and the gaseous.

A solid has a definite shape or *form*, and a definite *volume*. A *liquid* has no definite form, but has a definite *volume*. It can fill a vessel only to the extent of its volume and takes the shape of the containing vessel so far as it fills it. *Gases* have neither a definite form nor a definite volume. They tend to distribute themselves in all directions and fill completely any vessel into which they are brought. Their only boundaries are the containing walls.

9. Identifying Substances. — The different kinds of matter are identified by their properties or peculiarities. The more important of these are given in the table below.

Physical properties used in identifying substances:

SOLID STATE	LIQUID STATE	GASEOUS STATE
Density or relative weight;	Density or relative weight;	Density or relative weight;
melting point;	freezing point;	
	boiling point;	condensing point;
luster, hardness;		
color, taste, or smell;	color, taste, or smell;	color, taste, or smell;
solubility.	solubility.	solubility.

Chemical properties used in identifying substances:

Reactions with air or oxygen;
Reactions with water;
Reactions with acids or bases;
Actions peculiar to the substance or its constituents.

SUMMARY

Chemical changes involve changes in the identity of the material. The composition of the substance is usually altered, and energy changes are also involved.

A **compound** is a substance that can be separated into two or more substances. An **element** is a substance which has not been separated into other substances by man.

So far as known, matter cannot be created nor destroyed. (This statement is known as the **Law of the Conservation of Matter**.)

When a substance burns in air, it combines with oxygen, forming a new compound.

Lavoisier obtained oxygen from air by heating mercury in it and then decomposing the material produced.

EXERCISES

1. Air and water were formerly called elements. Why are they not now?

2. How could you prove that air contains oxygen?

3. What kind of change is involved in the withering of a leaf? Making cloth from wool? Baking bread? Burning coal? Extinguishing the fire?

4. Why is a burning candle extinguished by blowing?

5. Describe experiments that you performed in the laboratory which illustrate the difference between physical and chemical change.

6. Distinguish between the terms *element* and *compound*.

7. Give three examples of chemical change, each producing a different form of energy.

8. When 2 grams of a certain substance were heated, all the oxygen which the substance contained was given off, and a residue weighing 1.07 grams was left. Calculate the percentage of oxygen in the substance.

9. Why is the crushing of glass a physical change?

10. Name three chemical changes which occur in the kitchen; three physical changes.

11. What kind of changes are involved: in the digestion of food? The tanning of hides? The raising of your arm? The ripening of fruits? Paring of potatoes?

12. How would you show that lead, when heated in the air, combines with something to form a yellowish powder?

13. What is the difficulty in proving that the products formed by burning a candle weigh more than the candle?

14. What always happens when a substance burns in air?

15. How did the failure of the earlier investigators to use a balance prevent them from finding the true explanation of burning?

Volume
Pressure
Temperature

CHAPTER II

GASES AND THEIR MEASUREMENT[1]

10. Gas Pressure. — The peculiar properties of gases are due to the fact that the particles composing them are at considerable distances from each other and are in rapid motion. As these particles pelt against the walls of the containing vessel, they exert a pressure on the walls. If a gas is compressed into a smaller space, more particles will strike a square inch in a given time, and so the pressure measured in pounds per square inch is increased. The increasing pressure of the air in a bicycle pump, as the piston is forced down, illustrates this. If a gas is heated without being allowed to expand, its pressure on

FIG. 2. — STEAM GAUGES.

[1] If the instructor prefers, this chapter may be introduced later or used for reference in connection with the laboratory work, without interfering with the continuity of the course.

the walls of the vessel containing it will be increased, because the heat increases the speed of the particles.

The air which surrounds us is compressed by the weight of the atmosphere above it. The pressure due to the weight of atmosphere is about 15 pounds per square inch at sea level and is less at higher altitudes. It is not, however, a constant quantity, but varies with weather conditions. While the pressure of confined gases, like steam or compressed air, is measured by a pressure gauge (Fig. 2), atmospheric pressure is measured by the height of the column of mercury that it supports in a barometer (Fig. 3).

The barometer consists of a tube which has been entirely filled with mercury and then inverted into a reservoir of the same liquid. A pressure of 14.7 pounds per square inch is equal to the weight of a column of mercury 1 in. square, and 30 in. or 760 mm. high. As the gases whose volume we measure in the laboratory are usually subject to atmospheric pressure, gas pressures in chemical work are usually expressed in *millimeters of mercury* instead of pounds per square inch.

FIG. 3. — BAROMETER. *a*, Section; *b*, External view.

11. Effect of Temperature and Pressure Changes on Volumes of Gases. — The measurement of the volume of gases usually involves *a correction of the gas volume.* This is necessary because the volume of a given quantity of gas is considerably affected by even slight changes in temperature and

pressure. If the room gets warmer, the volume will be larger; if it gets colder, the volume will be less. Changes in atmospheric pressure will also cause the volume to vary. An increased pressure will mean a diminished volume, and a decreased pressure an increased volume.

The measurement of gases in experiments like the analysis of air will be of little value for accurate work unless account is taken of the temperature and pressure changes. For this reason it becomes necessary to know to what extent these affect the volumes. This is not a difficult matter, for it is found that all gases contract or expand to almost exactly the same degree when they are subjected to the same changes. This regularity is somewhat surprising. A similar thing is not at all true for solids or liquids. Any observed regularity of this sort is called a *law*.

12. Charles' Law. — It is found that if a certain quantity of any gas is made to have a temperature of 0° C., and then is warmed one degree, the gas expands $\frac{1}{273}$ of its volume. Warmed to 10°, it expands $\frac{10}{273}$ of its volume. Heated to 273°, its volume will be doubled. On cooling the gas, we find that it contracts $\frac{1}{273}$ *of its volume at 0° C* for each degree. At $-273°$ C. the volume of the gas would be zero, *if contraction continued at the same rate.* As a matter of fact, all known gases become liquids before this temperature is reached.

This point, $-273°$ C., has been selected as the zero of another temperature scale known as *absolute temperature* (Fig. 4). Since the size of the absolute degree is the same as the Centigrade degree, and since the absolute zero is 273 degrees below the Centigrade zero, a Centigrade temperature is changed to an absolute temperature by adding it, algebraically, to 273. Thus, 24° C.

becomes 297° abs. (273 + 24); − 12° C. becomes 261° abs. (273 − 12).

The general statement of the relation between the volume of a gas and its temperature is known as *Charles' Law*. Charles' Law may be stated thus:

The pressure remaining the same, the volume of a gas varies directly as the absolute temperature.

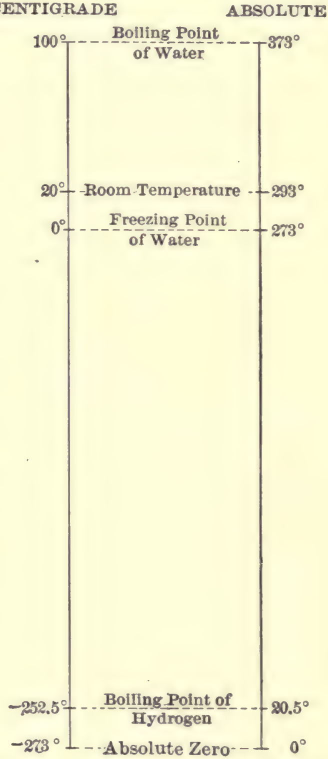


FIG. 4.— CENTIGRADE AND ABSOLUTE TEMPERATURE SCALES.

13. Use of Charles' Law in correcting Gas Volumes. — By using this law we can calculate what will be the volume of a gas at a temperature differing from that under which it is measured. For example, a quantity of air measures 25.6 c.c. at a temperature of 21° C. Find its volume at 0°.

$$21° \text{ C.} = 294° \text{ abs.}$$
$$0° \text{ C.} = 273°.$$

If the temperature of the gas were actually changed from 294° to 273°, it would be cooled, and would therefore contract. The volume at 273° will be less than the original volume. The fraction of the original volume will, therefore, be $\frac{273}{294}$ of its former volume. Hence:

$$x = 25.6 \text{ c.c.} \times \tfrac{273}{294}$$
$$= 23.7 \text{ c.c.}$$

14. Correction for Temperature. — The temperature of 0° C. (= 273° abs.) is chosen as the standard temperature for the measurement of gas volumes. The operation of finding the volume at the standard temperature is called *correcting* the volume *for temperature.* Sometimes it is necessary to find the volume at a temperature other than the standard temperature. The operation is a similar one.

Example: A quantity of gas has a volume of 75 c.c. at a temperature of 24°. What will be its volume at 100°?

Since the temperature is increased, the volume will also be increased. The fraction by which the original volume is to be multiplied is therefore greater than one.

$$\begin{aligned} x &= 75 \text{ c.c.} \times \tfrac{373}{297} \\ &= 94.2 \text{ c.c.} \end{aligned}$$

15. Boyle's Law. — Experiment shows that if the pressure on any gas is doubled and the temperature kept constant, the resulting volume will be one half the original volume. Under a pressure three times as great, the volume is one third. If the pressure is made one third the original pressure, the volume will become three times the original volume. In general, the greater the pressure, the less the volume in a proportional degree. This generalization, known as Boyle's Law, is usually stated thus:

The temperature remaining the same, the volume of a gas varies inversely as the pressure exerted upon it.

16. Use of Boyle's Law in the Correction of Gas Volumes. — Boyle's Law, like Charles' Law, enables us to calculate the volume of a given quantity of gas under new conditions. For example, a quantity of gas has a volume of 120 c.c., the barometer standing at 740 mm. What will be the volume when the atmospheric pressure has increased until the barometer stands at 760 mm.?

The numbers 740 mm. and 760 mm. are measures of the two pressures. The new volume will be found by multiplying the original volume by the ratio of these two numbers. It is apparent that the gas will be subjected to a greater pressure under the new condition. According to the law, its volume will be less. The fraction will therefore have the less number as the numerator. Hence:

$$\begin{aligned} x &= 120 \times \tfrac{740}{760} \\ &= 116.8 \text{ c.c.} \end{aligned}$$

17. Correction for Pressure. — The standard pressure for measuring gases is the pressure that the atmosphere exerts when the barometer stands at 760 mm. This is the average height of the barometer at sea level. The operation of finding the volume of a gas at this pressure is called *correcting the gas for pressure.* The volume of a gas at any pressure whatever is found in a similar manner.

Example: A quantity of air measures 82.2 c.c. at 520 mm. pressure. What will be the volume at 800 mm., the temperature remaining constant?

It is evident that the resulting volume will be less than the original, since the pressure under the new condition is increased. Hence the ratio by which the original volume is multiplied must be less than one.

$$\begin{aligned} x &= 82.2 \times \tfrac{520}{800} \\ &= 53.4 \text{ c.c.} \end{aligned}$$

18. Simultaneous Correction for Temperature and Pressure. — These two corrections can be carried out in one arithmetical operation, for the temperature effect and the pressure effect are entirely independent of each other. For example, a quantity of gas measures 206 c.c. at a temperature of 22° and a pressure of 750 mm. What will be the

volume of the gas under standard conditions of temperature and pressure?

$$x = 206 \times \underset{\text{Temperature correction}}{\tfrac{273}{295}} \times \underset{\text{Pressure correction}}{\tfrac{750}{760}}$$
$$= 188.1 \text{ c.c.}$$

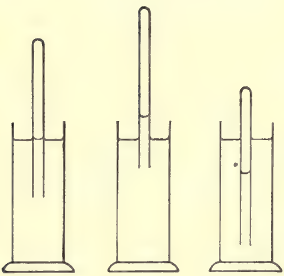


FIG. 5. FIG. 6. FIG. 7.

19. Correction for Difference in Level. — Gases are usually measured in bottles or tubes that stand over liquids. The liquid, as a rule, is either water or mercury. In order that the pressure of the gas inclosed under these conditions shall be equal to the atmospheric pressure, the levels of the liquid outside and inside the tube must be the same (Fig. 5). This condition is usually realized by adjusting the apparatus. Sometimes this is impossible, and then it is necessary to correct for the difference in level. This is done by adding to or subtracting from the height of the barometer a suitable number. When the inside level is the higher, the pressure on the inclosed gas is less than atmospheric (Fig. 6), for part of the atmospheric pressure is used in supporting the column of liquid in the tube; when the inside level is the lower, the pressure is greater than atmospheric (Fig. 7). For mercury, the actual difference in millimeters is added or subtracted; for water, one

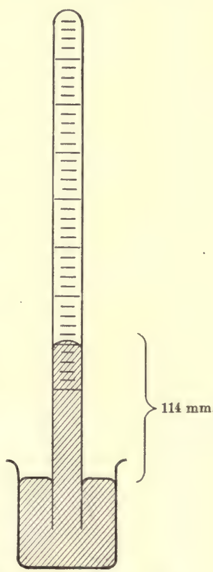


FIG. 8.

thirteenth of this value is used, since water is about one thirteenth as heavy as mercury.

Example: A volume of gas is inclosed in a tube over mercury (Fig. 8). The volume of gas measures 68.3 c.c., and the level of the mercury inside the tube is 114 mm. *above* the level in the dish. The thermometer reads 20° C. and the barometer 766 mm. Find the volume of the gas at standard conditions.

The corrected pressure is found by *subtracting* 114 mm. from 766 mm.,

$$766 - 114 = 652 \text{ mm.}$$

The gas volume will be corrected to standard conditions as follows:

$$\begin{aligned} x &= 68.3 \times \tfrac{273}{293} \times \tfrac{652}{760} \\ &= 54.6 \text{ c.c.} \end{aligned}$$

20. Correction for Pressure of Water Vapor. — When a gas is confined over water, some of the water evaporates and mixes with the gas. In such a case the pressure of the gaseous mixture consists of two parts, one due to the gas itself and the other due to the water vapor. The total pressure is the sum of these two pressures. The pressure due to water vapor, therefore, must be subtracted from the observed barometric pressure in order to determine the actual pressure of the dry gas. The pressure due to water vapor depends only on temperature, and not on any other conditions of the experiment. It is always the same for the same temperature, provided the gas is saturated with water vapor. Tables of these values for different temperatures have been prepared as the result of careful experiments. (See page 21.)

Corrections for difference in level and for the pressure of the water vapor (which is sometimes called *aqueous*

tension) are both pressure corrections. They are made by adding to or subtracting from the observed barometric pressure suitable numbers. These corrections are parts, then, of the pressure correction.

Example: 24.6 c.c. of nitrogen is contained in a tube over water. The level of the water inside the tube is 27 mm. above the outside level. The barometer stands at 762 mm., and the thermometer at 23°. What is the corrected pressure? On consulting a table we find that the pressure of aqueous vapor at 23° is approximately 21 mm. The corrected pressure is therefore:

$$762 - \underset{\text{in level}}{\overset{\text{Difference}}{\tfrac{27}{13}}} - \underset{\text{tension}}{\overset{\text{Aqueous}}{21}} = 739 \text{ mm.}$$

21. The following example will illustrate in full the operation of correcting gas volumes:

Volume of air	79.3 c.c.
Pressure uncorrected	764 mm.
Temperature	21° C.
Difference in water level (Fig. 6) .	+ 41 mm.
Aqueous tension at 21°	18 mm.
Corrected pressure . 743. .	
Corrected volume of air . . .	

The corrected pressure is

$$764 - \underset{\text{in level}}{\overset{\text{Difference}}{\tfrac{41}{13}}} - \underset{\text{tension}}{\overset{\text{Aqueous}}{18}} = 743 \text{ mm.}$$

$$21° \text{ C.} = 294° \text{ abs.}$$

If the temperature of the gas were changed from 294° absolute to 273° absolute, its volume would become less. Hence the ratio for the temperature correction is $\frac{273}{294}$.

Changing the pressure from 743 to 760 mm. would also tend to diminish the volume; the pressure correction ratio is, therefore, $\frac{743}{760}$. The final calculation is, then:

$$x = 79.3 \times \frac{273}{294} \times \frac{743}{760}$$
$$= 71.9 \text{ c.c.}$$

PROBLEMS

1. A quantity of hydrogen measures 53 c.c. at a temperature of 20°. What would it measure at 28°?

2. What volume would 60 c.c. of oxygen, measured at 17°, occupy at 0°?

3. Find the volume 65 c.c. of air would occupy, if its temperature were changed from − 13° to 23°.

4. 105 c.c. of oxygen at 27° were cooled to 17°. Find the new volume.

5. What volume would 39 c.c. of air occupy when its pressure changes from 768 mm. to 750 mm.?

6. 38 c.c. of gas were measured at 744 mm. pressure. Find the volume at 760 mm.

7. 80.2 c.c. of air stand in a tube, mercury levels adjusted; the barometer stands at 768 mm. The next day it reads 755 mm. What volume would the air then have?

8. 151 c.c. of nitrogen stand in a tube over water, with the inside level 139 mm. above the outside level. What volume would the gas have if the two levels were the same, the temperature being unchanged? The barometer stands at 754 mm.

9. How much would 52.2 c.c. of air measure if the barometric pressure changed from 750 mm. to 762 mm.? If the temperature also changed from 18° to 25°?

10. A quantity of air and water vapor, standing over water in a gas-measuring tube, levels adjusted, has a volume of 31.8 c.c. The temperature is 26°; the barometer stands at 737.6 mm. Correct the volume of air to standard conditions.

11. A quantity of air and water vapor in a tube over water, levels adjusted, measures 43 c.c. The thermometer stands at 24°, the barometer at 770 mm. Correct to standard conditions.

In the following cases correct the volume to standard conditions:

	Volume	Conditions	Temperature	Barometer
12.	152 c.c.	Over mercury; levels the same.	27°	755 mm.
13.	1.26 c.c.	Over water; levels the same.	20°	748 mm.
14.	210 c.c.	Over water; inside level 80 mm. above outside level.	22°	764 mm.
15.	15.2 c.c.	Over mercury; inside level 30 mm. above outside level.	21°	760 mm.
16.	129 c.c.	Over water; levels the same.	17°	770 mm.

17. A volume of gas (dry) measures 58.5 c.c. at a temperature of 183° and a barometric pressure of 759 mm. Find the volume of the gas under standard conditions.

216. c.c
22.° C.
295.° abs
764. mm · 764-19.7
19.7
80. mm
798.3 mm

Pressure of Water Vapor or Aqueous Tension

(in millimeters of mercury)

Temperature	Pressure	Temperature	Pressure
10.0° C.	9.2 mm.	20.0° C.	17.4 mm.
10.5	9.5	20.5	17.9
11.	9.8	21.	18.5
11.5	10.1	21.5	19.1
12.	10.5	22.	19.7
12.5	10.8	22.5	20.3
13.	11.2	23.	20.9
13.5	11.5	23.5	21.5
14.	11.9	24.	22.1
14.5	12.3	24.5	22.8
15.	12.7	25.	23.5
15.5	13.1	25.5	24.2
16.	13.5	26.	25.0
16.5	14.0	26.5	25.7
17.	14.4	27.	26.5
17.5	14.9	27.5	27.3
18.	15.4	28.	28.1
18.5	15.9	28.5	28.9
19.	16.4	29.	29.8
19.5	16.9	29.5	30.7
		30.	31.6

Charles Law All gases have the sa[me]
[illegible] temp. and pressure

Charles's Law
The pressure remaining the same, the volume of a gas varies directly as temperature.

Boyle's Law
The temp remaining the same, the vol[ume of] a gas varies inversely as the pressure.

CHAPTER III

OXYGEN

22. Preparation. — In 1774, Priestly obtained oxygen from a red powder prepared by heating mercury in the air. When this powder is heated at a temperature somewhat

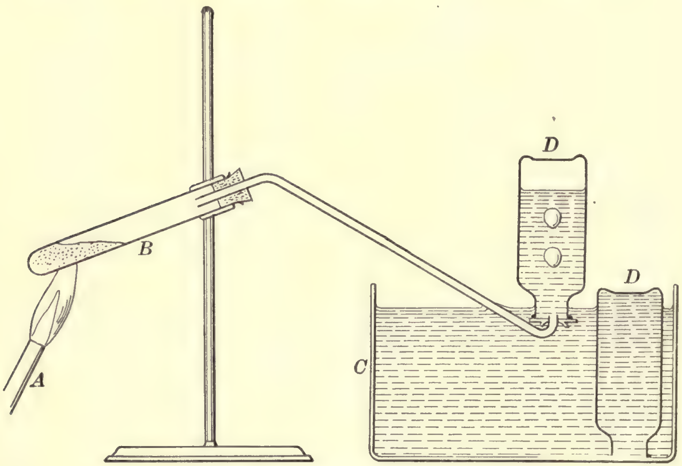


Fig. 9. — Preparation of Oxygen.

A, Bunsen burner; *B*, tube containing potassium chlorate and manganese dioxide; *C*, pneumatic trough; *D*, *D*, bottles for collecting the gas.

higher than that at which it was prepared, it is decomposed into a gas (oxygen) and metallic mercury.

When pure oxygen is desired in quantity, it is sometimes prepared from potassium chlorate (Fig. 9), a compound of potassium, chlorine, and oxygen; this, when

heated, melts and gives oxygen gas and a residue of potassium chloride. In the laboratory it is customary to mix the potassium chlorate with manganese dioxide, as it is found that the decomposition is more regular and takes place at a lower temperature. A material which thus aids chemical action, without being permanently altered, is called a *catalytic agent.* To free the oxygen from dust and other impurities, it may be allowed to bubble through water.

Oxygen is prepared from water on a commercial scale by passing an electric current through it (§ 33).

23. Physical Properties. — Pure oxygen is a gas without color, taste, or odor. It is slightly more dense than air. It dissolves somewhat in water; under ordinary conditions, 100 volumes of water dissolve 3 volumes of oxygen. If ordinary faucet water be allowed to stand in a glass, or if the water be warmed, bubbles will be observed clinging to the sides of the glass before the water actually boils. Such bubbles are largely oxygen, which was dissolved in the water.

If cooled sufficiently, oxygen condenses to a pale blue liquid, and, on still further cooling, solidifies.

24. Chemical Properties. — The most noticeable chemical property of oxygen is its *tendency to combine with other elements.* At ordinary temperatures, it does not readily react with many substances, but at higher temperatures its action is rapid, and is usually accompanied by heat and light. Nearly all the elements combine readily with oxygen to form compounds known as *oxides.*

25. Combustion is a chemical action by which heat and light are evolved. Lavoisier, in 1786, was the first to explain *ordinary burning* as the combining of a substance

with oxygen. When the action takes place rapidly, the increase in temperature is appreciable, and light may result (Fig. 10). Thus, when a piece of coal burns, the carbon of the coal combines with the oxygen of the air to form carbon dioxide, a gas which passes off unseen; at the same time a considerable quantity of heat is evolved, and the neighboring particles of fuel become red-hot.

As the air is only about one fifth oxygen, substances do not burn as readily in it as in pure oxygen. A glowing

Fig. 10.—Phosphorus Burning in Oxygen.

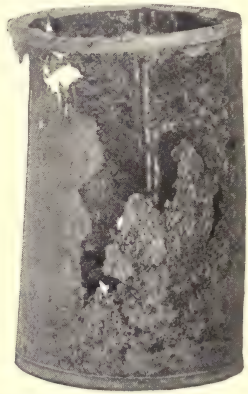


Fig. 11.—Rusting of Iron.

splinter plunged into oxygen bursts into flame. Charcoal glows much more brilliantly in oxygen than in air. Sulphur burns in air with a pale blue flame, in oxygen vividly. Iron burns in oxygen with dazzling scintillations.

Since all common cases of burning require the presence of oxygen, the gas is said to *support combustion.*

26. Slow Oxidation. — Oxidation is not always accompanied by light or even by noticeable heat. Thus, when iron rusts (Fig. 11), it slowly combines with oxygen;

when wood decays, the materials produced are nearly the same as are formed when it burns. The total amount of heat is the same in both cases, but in the decay the change takes so long a time that there is no appreciable change of temperature. A match gently rubbed in the dark appears luminous without flaming. Such changes as rusting and decay are termed slow oxidation. As distinguished from burning, *slow oxidation is the combination of a substance with oxygen without the accompaniment of noticeable light or heat.*

27. Kindling Temperature. — We know that some substances burn more easily than others; heat must be applied to raise them to the temperature at which they *take fire* and begin to burn. This *kindling temperature* varies with different substances; the kindling temperature of phosphorus is but little above the ordinary laboratory temperature, but the temperature produced by the burning is much higher. If the burning material is a good conductor, as iron, the heat is conducted away so rapidly that the temperature falls below the kindling temperature and the fire goes out. Similarly, gas lighted above an iron gauze (*a*, Fig. 12) does not catch fire below the gauze, because the heat of the flame is conducted away by the iron. When the material is in small pieces, or is powdered, there is more surface exposed to the oxygen, so that the burning can proceed more rapidly; thus, finely divided iron will burn when sprinkled into a Bunsen flame, since there is a large surface exposed, and there is no large mass to withdraw the heat. In the case of iron,

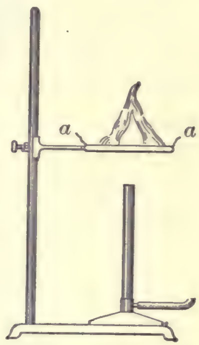


FIG. 12.

the oxide produced is a solid which remains, and may cover the iron and prevent its coming in contact with the oxygen, thus stopping further action. Iron is artificially coated with a thin, regular film of one of its oxides (§ 405) to protect the sheet against rusting. Iron so protected is known as Russia iron.

28. Spontaneous Combustion. — Many oils, such as are used in paints, absorb oxygen. Linseed oil absorbs oxygen and forms a tough, resinous substance, the skin seen on the surface of paint. On painted surfaces, this skin holds the coloring matter and protects the material beneath. The heat generated in its formation is dissipated in the air. If rags or waste, greasy with such oils, are left lying about, oxidation takes place, and since the materials are usually poor conductors and their form prevents sufficient circulation of the air to keep them cool, the heat does not escape, but accumulates until the temperature rises high enough for the stuff to take fire. Coal dust in coal bunkers often becomes ignited in this way. Such cases of burning are often called spontaneous combustion. *Spontaneous combustion is an active burning started by the accumulation of the heat of a slow oxidation.* It is especially liable to occur in poorly ventilated places with greasy cloths and waste, such as are used about machinery.

29. The Bunsen Burner. — This burner is a device for adjusting the proportions of fuel gas and air so as to get the combustible mixture giving the hottest flame. The bunsen burner was the first successful device for efficiently utilizing gas for heating and its principle is employed in all gas heaters.

When the burner is in use, gas enters the barrel through the spud (Fig. 13), and mixes with a supply of air partially

Robert Wilhelm Bunsen (1811–1899) was born in Göttingen and educated in its university. He served as professor in several German universities. At Heidelberg he had a career of nearly fifty years as a great teacher and brilliant investigator. His researches led to the acceptance of the idea of radicals existing in compounds. Many of his simple and efficient laboratory devices are in use to-day, notably the Bunsen burner. Bunsen may be regarded as the founder of modern gas analysis. His greatest work was the discovery, with Kirchhoff, of spectrum analysis. This proves useful in the detection of known elements, and has led to the discovery of new ones. By its means Bunsen found cæsium and rubidium.

sufficient for complete combustion. The mixture rises to the top of the barrel, where it is ignited, drawing an additional supply of oxygen from the surrounding air. The air enters the holes at the base of the barrel because the gas as it issues from the spud at a high speed causes a partial vacuum in the barrel, which the air rushes in to fill.

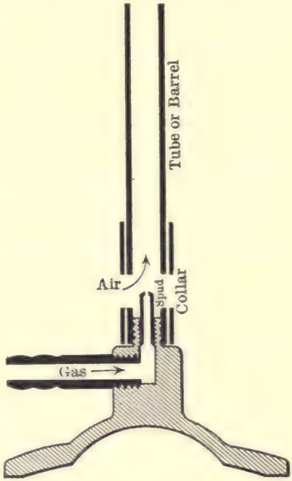


FIG. 13. — SECTION OF BUNSEN BURNER.

The supply of gas entering the barrel is regulated by varying the size of the opening in the supply pipe. The supply of air is regulated by turning the ring or collar so as to vary the size of the holes through which the air enters the barrel. If the gas pressure is low, the mixture of gas and air may burn downward more rapidly than it issues from the barrel. In this case the flame *strikes back* to the spud, where incomplete combustion takes place. This produces a disagreeable odor. Sometimes the base becomes sufficiently hot to melt the rubber hose, and the escaping gas catches fire.

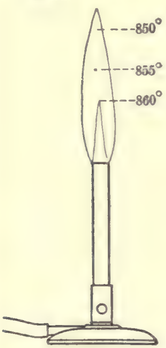


FIG. 14.

The extreme tip of the outer flame causes many substances to oxidize when they are heated in it, and is consequently called the *oxidizing flame.* The portion of the flame having the *highest temperature* is just above the inner cone (Fig. 14).

The combustion in the bunsen flame is more rapid

than that in the ordinary gas flame, since the fuel does not get far from the burner before burning. Therefore, the flame is smaller and *for this reason* hotter. It is not luminous, owing to the rapid and complete burning and to the dilution of the materials by the nitrogen.

30. Occurrence of Oxygen. — Oxygen is the most abundant element: about one half of the solid crust of the earth, eight ninths of the water, and one fifth of the air, is oxygen. Limestone, marble, clay, quartz, and sand are nearly half oxygen, and it comprises a large proportion of animal and vegetable matter.

31. Oxygen in Relation to Life. — All animals need oxygen for the carrying on of their life processes. The air supplies this needed oxygen to land animals, while fishes obtain it from the dissolved oxygen which water absorbs from the air. The oxygen is taken in during the process of breathing, absorbed by the blood, and carried to all parts of the body. The various tissues are slowly oxidized, heat being liberated by the action. It is this heat which keeps the bodies of the higher animals continually warmer than the surrounding air. One of the chief products of this oxidation is carbon dioxide, which is carried by the blood to the lungs and there exhaled.

Plants feed on carbon dioxide, which they absorb from the air through their leaves. The carbon of this compound is retained in the tissues of the plants, but the oxygen for the most part is returned to the air. Thus plants and animals mutually assist in keeping the quantity of oxygen in the air constant. Plants also inhale a small quantity of oxygen directly from the air, and exhale a little carbon dioxide.

32. Ozone. — If electric sparks are passed through oxygen, or better, if it be subjected to a "silent discharge" of electricity, it is changed to another form of oxygen, which is more active, and which has the irritating smell noticeable where electrical machinery is working. This form of oxygen is known as *ozone*. Ozone is also produced by the slow oxidation of phosphorus in moist air.

When ozone is heated to 270° C. it is changed to oxygen, two volumes of ozone yielding three volumes of oxygen, so that the ozone is one and a half times as dense as oxygen.

Silver, which is not affected by ordinary oxygen, is rapidly darkened (oxidized) by ozone. Many colors are bleached by it.

Improved devices for the production of electricity have cheapened the cost of ozone, so that it is used for purifying the water supply of large cities, as Paris and Petrograd. The ozone is produced by electric discharges in special apparatus known as ozonizers, and then allowed to bubble up through long cylinders, to which water is admitted at the top. These streams of minute bubbles of ozone destroy all forms of bacterial life.

Recent experiments have used ozone for the purification of the air of school rooms and of places for public assemblage. Although there was no doubt as to the germicidal action of the ozone and its removal of objectionable odor, the results in other ways were not altogether satisfactory.

The atmosphere sometimes contains a small amount of ozone near the seashore and in the open country. The bleaching of flax and linen by exposing the goods on the grass in the early morning has been attributed to the ozone dissolved in the dew.

SUMMARY

Oxygen is prepared by :

(a) decompositon of mercuric oxide ;
(b) decomposition of potassium chlorate ;
(c) electrolysis of water.

Oxygen is 1.1 times as heavy as air. Liquid oxygen boils at −182° and solidifies below −218°.

Oxygen **combines** with nearly all other elements.

An **oxide** is a compound of oxygen and another element.

A **catalytic agent** is a material which aids chemical action without itself being permanently changed.

Combustion is a chemical action in which heat and light are evolved.

Oxidation is the combination of a substance with oxygen.

Ordinary burning is an oxidation accompanied by noticeable heat and light.

Slow oxidation is the combination of a substance with oxygen without the accompaniment of noticeable light or heat.

The **kindling temperature** of a substance is the lowest temperature at which it takes fire and burns.

Ozone is a more active form of oxygen.

EXERCISES

1. How would the production of oxygen be affected if potassium chlorate were heated without a catalytic agent?

2. How would you prove that water from a stream or a pond contains dissolved oxygen?

3. Name the product formed by burning each of the following: carbon, iron, sulphur, tin, magnesium, and phosphorus.

4. What is ordinary burning?

5. What would happen if a lighted candle were lowered into a jar of oxygen? Why?

6. Why does the throwing of a rug around a burning dress extinguish the flame?

7. Why should not the term combustion be applied to a case of slow oxidation?

8. Explain the successive use of paper, wood, and coal in making a coal fire.

9. Explain why polishing stoves prevents rusting.

10. Explain why a candle goes out if a wire gauze is slowly lowered till it touches the wick.

11. Why may a spark in a flour mill produce an explosion?

12. Give a practical illustration of putting out a fire (*a*) by lowering the temperature of the burning material below its kindling point; (*b*) by the removal of the combustible material; (*c*) by cutting off the supply of oxygen.

13. State the conditions necessary for spontaneous combustion.

14. Why are metal cans provided for the oily waste in wood-turning shops?

15. Why should not greasy cloths be thrown into a closet?

16. Name two gases in the air that are required by plants? Which in the larger amount?

17. Account for the peculiar odor in the air after a thunderstorm.

18. Why is ozone used for the purification of water?

19. Why does blowing extinguish a candle?

20. Why does blowing on a fire make it burn more brightly?

21. In order to find the per cent of oxygen in air, the oxygen was absorbed by means of phosphorus, and the following data were obtained:

	With Oxygen	Oxygen Removed
Volume	99.8 c.c.	77.0 c.c.
Temperature	24°	19°
Barometer	763 mm.	750 mm.

The air stands over water, and the levels are adjusted in reading both volumes. Calculate the per cent of oxygen.

CHAPTER IV

HYDROGEN

33. Preparation by Electrolysis of Water. — If the two wires from a battery be placed in pure water, it will be found that practically no current passes. Water is a very poor conductor of electricity. If a small quantity of sulphuric acid is added to the water, the solution is a good

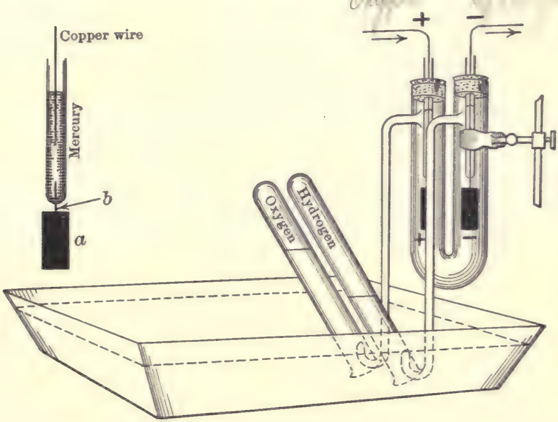


FIG. 15. — ELECTROLYSIS OF WATER.
a, platinum electrode; *b*, platinum wire fused through glass.

conductor. During the passage of the current, bubbles form at the ends of the wires; at the positive electrode (*anode*) small bubbles of oxygen appear; at the negative electrode (*cathode*) there is a rapid evolution of hydrogen (Fig. 15). If the volumes of the gases be compared, it will be found that there has been set free twice as much

hydrogen as oxygen. At the end of the experiment, the sulphuric acid is found unchanged in amount, though some of the water has disappeared. Another catalytic agent, for example, potassium hydroxide, sodium hydroxide, or sodium sulphate, might be used in place of the sulphuric acid. Commercially, potassium hydroxide is used. The electrolysis has converted a part of the water into oxygen and hydrogen, and the volume of the gases formed is very great compared with the volume of the water decomposed. The chemical change may be briefly represented by the word equation:

$$\text{water} \longrightarrow \text{hydrogen} + \text{oxygen}.$$

The arrow in such an expression is to be read *yields*, and the plus sign is to be read *and*.

34. Action of Metals on Water. — If a piece of potassium is placed on water, it skims back and forth over the surface, decomposing the water so rapidly that, if a large piece of the metal is used, the action is dangerously violent. A great deal of heat is generated, so that the hydrogen is set on fire (Fig. 16). When sodium is used, although the action is very rapid, the heat generated is not usually sufficient to ignite the hydrogen unless the water is warm, or the sodium is prevented from moving on the surface of the water.

The metal sets free only one half of the hydrogen of the water, and combines with the remaining half and with all of the oxygen, to form the hydroxide of the metal. The metallic hydroxide formed dissolves in the water in the vessel. The following word equations may be used to represent the reactions:

$$\text{potassium} + \text{water} \longrightarrow \text{potassium hydroxide} + \text{hydrogen}$$
$$\text{sodium} + \text{water} \longrightarrow \text{sodium hydroxide} + \text{hydrogen}.$$

Some of the other metals will also react with water. When calcium is used, the action is quiet, and not all of the calcium hydroxide dissolves. Magnesium will react rapidly only when the water is hot.

FIG. 16. — POTASSIUM ON WATER.

If steam is passed through a heated pipe filled with iron nails, an abundant supply of hydrogen can be obtained. The oxygen of the steam combines with the iron, according to the equation:

$$\text{iron} + \text{water (steam)} \longrightarrow \text{iron oxide} + \text{hydrogen.}$$

35. Replacement in Acids by Metals. — In the seventeenth century, Paracelsus observed that when iron dissolved in an acid a gas was evolved. All acids contain hydrogen that can be exchanged for a metal, and in a number of instances the hydrogen is liberated and can be obtained

free. Since the reaction takes place at ordinary temperatures and can be easily controlled, the most convenient method of preparing small quantities of hydrogen is to add a water solution of sulphuric acid to zinc (Fig. 17). While hydrogen is set free during the reaction, the zinc combines with the remaining part of the sulphuric acid and forms a new compound, zinc sulphate, which remains dissolved in the liquid in the generator:

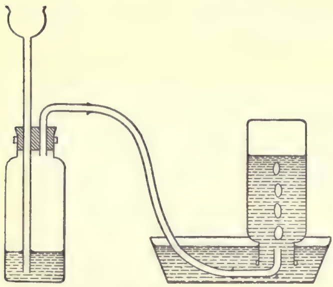


FIG. 17.—HYDROGEN GENERATOR.

$$\underbrace{\text{sulphuric acid}}_{\begin{cases}\text{hydrogen}\\ \text{sulphur}\\ \text{oxygen}\end{cases}} + \text{zinc} \longrightarrow \underbrace{\text{zinc sulphate}}_{\begin{cases}\text{zinc}\\ \text{sulphur}\\ \text{oxygen}\end{cases}} + \text{hydrogen.}$$

Sulphuric acid and zinc sulphate are compounds, and the words printed in small letters under each indicate of what elements it is composed. The rapidity of the action depends on the temperature, the concentration of the acid solution, the surface of the metal exposed, and the purity of the materials. Concentrated sulphuric acid should be diluted with from four to six times its volume of water. A catalytic agent, for example, carbon or copper, must be in contact with the zinc. Commercial zinc is generally sufficiently impure to give good results.

Other metals besides zinc and other acids besides sulphuric acid may be used for the preparation of hydrogen, but it is far from true that free hydrogen can be obtained by the reaction between *any* acid and *any* metal. Dilute solutions of either sulphuric or hydrochloric acid are usually employed, with either zinc or iron.

36. Physical Properties. — Hydrogen is a gas without color, taste, or odor. When commercial zinc and acid are used in its preparation, impurities are carried along with the hydrogen, giving it a peculiar, disagreeable odor. If iron is used instead of zinc, the unpleasantness of the odor is more noticeable. Hydrogen is scarcely soluble in water. It is the lightest substance known; 1 liter of hydrogen weighs 0.09 of a gram. The rate of escape of gases through small apertures (effusion of gases) varies inversely as the square roots of their densities. Hydrogen, being the lightest gas, escapes more rapidly than any other. A small rubber balloon filled with hydrogen collapses more rapidly than a similar balloon filled with illuminating gas.

Certain metals, as platinum and palladium, have the power of absorbing large volumes of hydrogen. The hydrogen is expelled when the metal is warmed. Such an absorption of gas by a solid is called *occlusion*. While the gas is being absorbed, considerable heat is set free, and, if oxygen is present, the hydrogen may ignite. The occluding action of such a metal is utilized in self-lighting gas burners and cigar lighters.

Hydrogen has been liquefied and solidified. The liquid is one fourteenth as dense as water, and is the lightest liquid known.

CHEMICAL PROPERTIES

37. Combustibility. — The most important chemical property of hydrogen is its combustibility. Cavendish, in 1783, showed that hydrogen burning in air formed water. The water formed by the combustion of hydrogen usually passes off unnoticed as steam, but it may be condensed on a cool surface (Fig. 18). The flame of hydrogen is blue, almost invisible in the daylight, and is very hot. Hydro-

gen in burning gives as much heat as about 5 times its weight of coal.

If hydrogen and oxygen are mixed, and the mixture is raised to its kindling temperature, or if an electric spark is passed through the mixture, combustion takes place throughout the entire mass almost instantaneously, producing a sudden increase in volume. Such a rapid com-

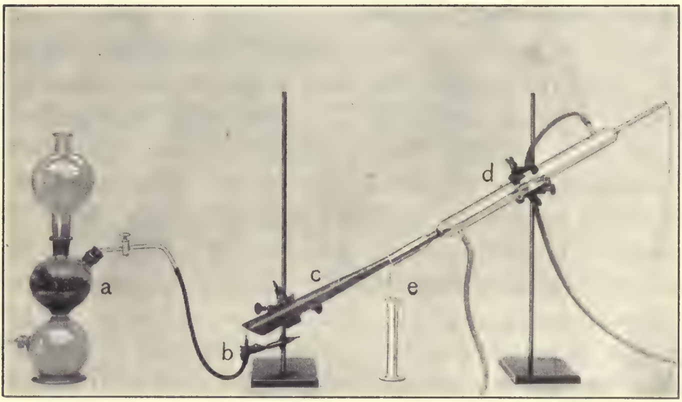


FIG. 18. — FORMATION OF WATER.

a, hydrogen generator; *b*, jet of burning hydrogen; *c*, metallic cone; *d*, glass condenser; *e*, string along which condensed water runs into graduate.

bustion, accompanied by a sudden increase in pressure, is termed an *explosion*. A jet of oxygen can be made to burn in hydrogen, thus showing that the two gases take equal part in the action. $2H_2 + O_2 \rightarrow 2H_2O$

38. Reducing Action. — Hydrogen will take oxygen from many oxides when they are heated in it (Fig. 19), forming water (steam) and leaving the metal free:

copper oxide + hydrogen ⟶ water + copper.

$CuO + H_2 = H_2O + Cu$

This process of taking oxygen away from a substance is called *reduction*, and substances that take oxygen away are called *reducing agents.* As the hydrogen is *oxidized* in the process, we see that oxidation and reduction go on together and are opposite processes. Hydrogen is one of the most energetic reducing agents. Energy equivalent to about 3800 calories of heat must be used to decom-

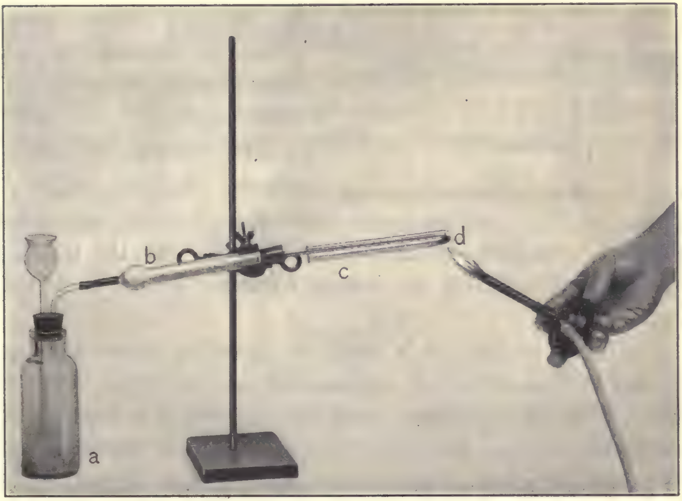


FIG. 19. — REDUCTION OF HOT COPPER OXIDE BY HYDROGEN.
a, hydrogen generator; *b*, drying tube; *c*, test tube; *d*, copper oxide.

pose one gram of water. The amount of heat given off during the formation of water explains the stability of water.

39. Uses. — The low density of hydrogen permits its use in balloons. The high temperature of the flame is used in the oxy-hydrogen blowpipe. This consists of two tubes as shown in Fig. 20. The hydrogen passes

through the outer tube and is lighted at the tip; then the oxygen is turned on through the inner tube. As the gases are supplied under pressure, a blast is formed which gives an intense heat. This flame is used to melt platinum and other refractory materials, such as aluminum oxide, during the manufacture of artificial rubies and sapphires. When a stick of quicklime is placed in the tip of the flame, it does not melt, but becomes white-hot, giving an intense white light. This is known as the Drummond, lime, or calcium light.

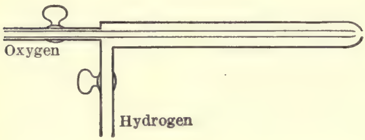


FIG. 20. — OXY-HYDROGEN BLOWPIPE.

The process of joining sheets of lead, edge to edge, known as lead-burning, consists in laying the sheets in the position desired and melting the edges together with a hydrogen flame.

Ordinary water gas is made by blowing steam through a mass of incandescent anthracite coal, or coke. It contains 50% of hydrogen and is suitable for burning to produce heat, but the straight, or unenriched, water gas has no practical value as an illuminant. Nearly three fourths of the illuminating gas used in this country is *enriched* water gas (§ 335) and contains about 38% of hydrogen.

40. Hydrogenation of Oils. — Large quantities of hydrogen are consumed in the hydrogenation of oils. In the presence of a suitable catalytic agent, for example, finely divided nickel (obtained by the reduction of nickel oxide), hydrogen enters into combination with cottonseed oil and converts it into a product resembling lard. This product is edible and is sold extensively as a lard substitute. By a similar process, fish oil can be made to lose its disagree-

able odor and be converted into a fat suitable for use in making hard soap.

SUMMARY

Hydrogen is commonly **prepared** by:

(1) the electrolysis of water (commercial method);
(2) the reaction between water and a metal;
(3) replacement in an acid by a metal. This is the most convenient method.

A liter of hydrogen, under standard conditions, weighs 0.09 gram. A liter of water at 20° dissolves 18.2 c.c. of hydrogen. Liquid hydrogen boils at − 252.5° and solidifies at − 259°.

Hydrogen **burns** in oxygen or air, forming water. It is a powerful **reducing agent**. The chief **uses** of hydrogen are for balloons, for fuel, and for the hydrogenation of oils.

EXERCISES

1. What would be the result of collecting together the gases formed by the electrolysis of water and applying a light to the mixture? There

2. Would you use water or sand to extinguish burning sodium? Why?

3. Would you use zinc or iron for making hydrogen to fill a large balloon? Why?

4. What becomes of the product, other than hydrogen, formed when zinc and sulphuric acid react?

5. Is water an oxide?

6. How would a soap bubble behave if filled with hydrogen instead of air?

7. Why do toy balloons filled with hydrogen collapse in a short time?

8. Would a bottle of hydrogen, closed with an ordinary cork, remain full after standing overnight?

9. Would a bottle of hydrogen remain full if left inverted overnight with its mouth under water?

10. Why must all the air be expelled from a hydrogen generator before the gas is lighted at the end of the delivery tube?

11. Should vessels containing hydrogen be kept mouth upward or mouth downward?

12. Why would pure hydrogen not make a good illuminating gas?

13. Could hydrogen be substituted for illuminating gas in an ordinary gas stove?

14. What is formed when iron oxide is heated in a current of hydrogen?

15. Would a Welsbach burner supplied with hydrogen give light?

16. Why is hydrogen called a reducing agent?

17. What is lead burning?

18. By making use of hydrogen, how could you show that air contains oxygen?

19. Mention two ways in which the cheap production of hydrogen tends to decrease the cost of living.

CHAPTER V

COMPOSITION OF WATER AND COMBINING WEIGHTS

41. Analysis and Synthesis. — In the electrolysis of water, we showed that water could be separated into two parts hydrogen and one part oxygen by volume. Such a separation is called an *analysis*. The combining of these substances is called a *synthesis* of water.

42. Synthesis by Volume. — If known volumes of hydrogen and oxygen are introduced into a tube inverted over mercury, and exploded by an electric spark between platinum wires fused through the glass, it is found that the volumes of the gases uniting are two volumes of hydrogen to one of oxygen, and that any excess of either gas is left unchanged. It is only when two volumes of hydrogen are mixed with one of oxygen that the two gases totally disappear. A little mist is seen on the tube, which is the moisture formed, and the mercury rises and fills the tube. This, again, shows that water consists of two parts hydrogen and one part oxygen. Another form of apparatus (Fig. 21),

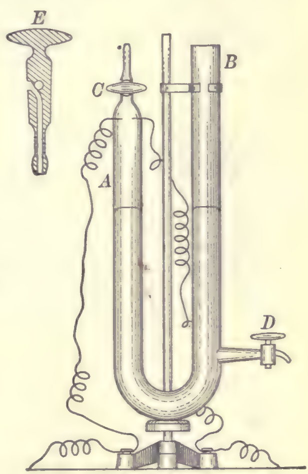


FIG. 21.

differing in the shape of the tube from that just described, facilitates the adjustment and reading of the mercury levels. Additional mercury, if needed, can be poured through the open arm *B*, and an excess can be drawn off through the lower stopcock *D*. The gases used in *A* can be drawn in easily through the three-way stopcock *C* shown in detail at *E*. If the tube *A* is provided with a heating device so that the temperature can be raised above 100° C., the volume of the steam can be measured. If the measurements are made at the same temperature and pressure, it will be found that *the volume of the steam is just equal to the volume of the hydrogen.*

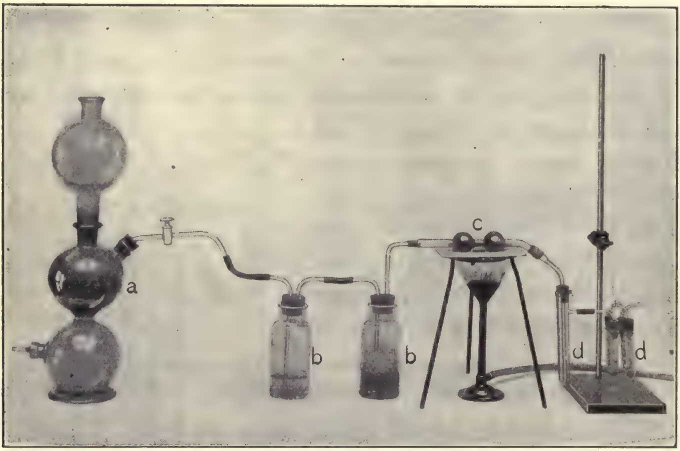


FIG. 22. — COMPOSITION OF WATER BY WEIGHT.

a, hydrogen generator; *b*, *b*, drying bottles containing concentrated sulphuric acid; *c*, ignition tube containing copper oxide; *d*, *d*, apparatus for collecting water formed.

43. Synthesis by Weight. — If dry hydrogen is passed over a weighed quantity of copper oxide which is heated, steam and copper result (Fig. 22). The water can be collected and weighed in a tube containing a drying agent.

John Dalton (1766–1844) was an English schoolmaster, investigator, and mathematician. Dalton's work led up to the fundamental ideas of modern chemistry.

He studied rocks, dew, the weather, and various phenomena, notably those of gases, which he pictured as made up of small, elastic particles. While the idea of atoms was not original with Dalton, he experimented and collected data which showed that the facts could be explained by what we now call the atomic theory.

The law of definite proportions and the law of multiple proportions are two of the most important chemical generalizations stated by Dalton in the development of his theory.

The weight lost by the copper oxide is the weight of the oxygen. The difference between the weight of the oxygen and the weight of the water formed is the weight of the hydrogen.

44. Law of Definite Proportions. — The ratio between the weights of the oxygen and hydrogen is found to be 7.94 : 1. This relation is unvarying. Experience has shown that *every compound has a definite composition by weight*. This is known as Dalton's first law, or the *law of definite proportions*.

45. Combining Weights. — Experience has shown that the knowledge of the composition by weight of chemical compounds is very useful. For example, we can determine what weights of substances are needed for a given chemical action, and what weight of the products will be formed. Moreover, a study of these weights reveals some surprising regularities. Let us consider a few simple cases. In the table below, in the OXYGEN column is given the weight of oxygen that combines with one part by weight of the substance in the first column. Similarly the columns SULPHUR and CHLORINE give the weights of these elements that combine with one part by weight of the element in the first column.

	OXYGEN	SULPHUR	CHLORINE
1 part hydrogen combines with	8.00	16.0	35.5
1 part carbon	2.66	5.33	11.8
1 part magnesium	.666	1.33	2.96
1 part calcium	.400	.800	1.77
1 part copper	.251	.502	1.11
1 part zinc	.246	.492	1.09
1 part mercury	.080	.160	.35
1 part silver	.074	.148	.33

The numbers vary considerably, and there seems to be little order about them. We have considered one part by weight of each material in the first column. We have used eight different units; a unit quantity of hydrogen, a unit quantity of carbon, and so forth. We notice that the weights in the sulphur column are double those in the oxygen column and weights in the chlorine column are nearly 4.44 times the oxygen weights.

This suggests the value of reducing all the ratios to a common standard, so that regularities will be apparent at a glance. Hydrogen enters into combination in the least part by weight of any of the elements.

Let us, therefore, use 1 for the combining weight of hydrogen.

If we took 1 part by weight (1 pound, 1 gram, or 1 unit of any kind) of hydrogen and combined it with oxygen, it would require 8 parts by weight, 8 pounds, 8 grams, or 8 of whatever units were chosen.

Now, 2.66 parts of oxygen combine with 1 part of carbon, so 8 parts of oxygen are needed to combine with 3 parts of carbon. These 3 parts of carbon, then, will combine with 1 part of hydrogen.

In the same manner we find that the 8 parts by weight of oxygen that will unite with 1 part of hydrogen, will combine with 20 parts of calcium, or 31.8 parts of copper, or 32.7 of zinc.

The 16 parts of sulphur that combine with 1 part of hydrogen will combine with just 3 parts of carbon (since 5.33 parts of sulphur combine with 1 part of carbon), or with 20 of calcium, or with 31.8 of copper.

Similarly we can find the weights of these elements, in the first column, that could unite with the 35.5 parts of chlorine which combine with 1 part of hydrogen. The weights are given in the table following.

	OXYGEN	SULPHUR	CHLORINE
1 part hydrogen will combine with	8	16	35.5
3 parts carbon	8	16	35.5
12 parts magnesium	8	16	35.5
20 parts calcium	8	16	35.5
31.8 parts copper	8	16	35.5
32.5 parts zinc	8	16	35.5
100 parts mercury	8	16	35.5
108 parts silver	8	16	35.5

Thus we see that the combining number is found to be the same for each of these elements, regardless of the other element in the compound. Experiment shows that 3 parts of carbon will combine with 1 part of hydrogen and that 20 grams of calcium or 32.7 grams of zinc are required to liberate 1 gram of hydrogen from water or any other hydrogen compound. From this it appears that each element enters into chemical action in a definite number of parts by weight, and if we establish these numbers on a relative scale, the number for an element is the same in all its compounds. This number is called the *equivalent* or *reacting weight* of the element.

46. Reacting Weight. — It is found that such a number can be assigned to every element. The number is found by determining the number of parts by weight of the given element which unite with, or replace, one part of hydrogen, or its equivalent. Thus we see that all reacting weights are relative numbers, and they refer or relate to the combining weight of hydrogen which is taken as unity.

It frequently happens that more than one reacting weight can be assigned to a given element. For instance, oxygen combines in two different proportions with hydrogen,

forming two different compounds. In water the ratio is 8 to 1, in the other compound the ratio is 16 to 1. *In such cases, one reacting weight is always a multiple of the other.*

47. Method of determining Reacting Weights. — The reacting weight is determined by an analysis of the hydrogen compound, if one exists. In some other cases the value is determined by finding the weight of the element that replaces 1 gram of hydrogen. In still other cases, the number expressing the weight of the element that combines with 35.5 grams of chlorine or 8 grams of oxygen is taken as the reacting weight.

SUMMARY

The composition of water can be shown by **analysis** and by **synthesis.** Two volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam.

Water consists of 1 part by weight of hydrogen combined with 8 parts of oxygen; and, since it always has this composition, it illustrates the **law of definite proportions**, that every compound has a definite composition by weight.

The number of parts by weight of an element which react with one part by weight of hydrogen, or its equivalent, is called the **reacting weight** of that element. When an element has more than one reacting weight, the numbers expressing these weights are always multiples of the smallest number.

EXERCISES

1. When sugar is heated sufficiently to char it, water is driven off. What two elements besides carbon must sugar contain?

2. Why does a thin film of water collect on the inside of a lamp chimney when the lamp is first lighted? Why does the moisture soon disappear?

3. Dry hydrogen was passed over heated copper oxide and the water formed was absorbed by fused calcium chloride. The following results were obtained:

Wt. of copper oxide tube before the experiment	70 g.
Wt. of copper oxide tube after the experiment	66 g.
Wt. of calcium chloride tube after the experiment . .	106.5 g.
Wt. of calcium chloride tube before the experiment . .	102 g.

From the above data calculate the weight composition of water.

4. 15 c.c. of oxygen were collected in a eudiometer over mercury. Dry hydrogen was passed into the eudiometer until the volume of the mixed gas was 22.4 c.c. A spark was then passed through the mixture. What gas was left in the eudiometer? How would you prove your answer? What would be the volume of the remaining gas?

5. Mention three ways by which water can be decomposed.

6. Describe an experiment that you could perform to illustrate the law of definite proportions.

7. How many grams of zinc are necessary for the production, by the action of hydrochloric acid on the metal, of 90 liters of hydrogen measured under standard conditions? (One liter of hydrogen weighs 0.09 gram.) 2632.5 gr.

8. What does the analysis of water show its composition to be by volume? 2 part

9. Mention two methods for the synthesis of water.

CHAPTER VI

WATER AND SOLUTION

48. Physical Properties. — Pure water is an odorless liquid. Small quantities appear to be colorless, although large masses show a distinct blue color. Water is usually taken as the standard in comparisons of physical properties of liquids and solids. The zero of the Centigrade thermometer registers the position of the top of the mercury column when the thermometer is placed in melting ice, and since a pure substance on being warmed always melts at the same temperature as that at which it would solidify if cooled, the zero of the Centigrade thermometer is the freezing point for water.

When pure water is heated to 100° C. under a pressure of 760 mm., it boils; if we continue to apply heat, the temperature does not rise higher, provided the steam is allowed to escape. The heat used in converting water into steam is known as the *heat of vaporization*, or the latent heat of steam; it is given off when the steam condenses. The heat used in changing ice to water is known as the *heat of fusion*. This is also latent heat, as it is given off when the water changes back to ice.

These quantities of heat are commonly measured in units known as *calories*. The calorie is the quantity of heat required to raise a gram of water 1° Centigrade. About 80 calories are required to change a gram of ice at 0° C. to water at 0° C., and 540 calories are required to change the same mass of water at 100° C. to steam at 100° C.

Both the freezing and boiling temperatures change when the pressure changes; increased pressure raises the boiling point and lowers the freezing point, in both cases tending to keep it in the *liquid* form. Any dissolved solid acts in the same way.

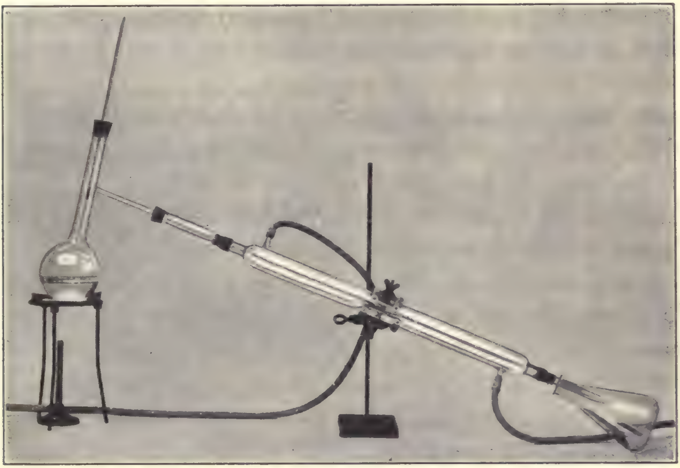


FIG. 23. — LABORATORY DISTILLATION.

49. Distillation. — All natural water contains dissolved substances. It is therefore necessary to boil water and then condense the steam to make it fit for chemical use; this process is called *distillation* (Fig. 23). Solids and liquids with boiling points much higher than that of water are left behind, as the temperature of the steam remains the same during the distillation. Materials having lower boiling points than water are distilled before or with the water; such impurities, ammonia for example, are found in the first portion of the condensed steam, and this is rejected.

Distillation consists in changing a liquid to a gas (vapor-

ization) and then cooling the gas so that it becomes a liquid again (condensation).

50. Steam. — Steam is water in the gaseous state; at ordinary pressure it condenses to liquid at 100° C.; if the pressure be removed, it remains in the gaseous condition at lower temperatures. The volume of steam is about 1600 times that of the water from which it was formed.

51. Ice. — If the temperature of water is lowered to 0° C., and energy removed, it solidifies to ice, usually crystallizing in hexagonal clusters of needles. There is considerable expansion during the solidification, and the density of the ice is only 0.91 that of water.

Water requires more heat to raise its temperature than do most substances; therefore its temperature changes more slowly than most objects, and large masses of water considerably affect the climate of the neighboring land.

52. Solution. — The most important property of water is its ability to dissolve substances. A substance is said to be in solution in a liquid when it is distributed uniformly through the liquid in a state of such fine division that its particles cannot be seen, and do not settle out on standing. When the particles are visible, the substance is said to be in suspension, and will usually settle quickly. A liquid used to dissolve a substance is called a *solvent;* the dissolved substance is termed the *solute.* A *solution* is a uniform mixture of these, which does not conform to the law of definite proportion. A solution will not boil at the same temperature as the solvent, nor will their freezing points be the same.

Water is a solvent for a large number of substances, and this use is most important. It dissolves both gases and

solids and mixes with many liquids. Liquids which do not separate but form a uniform mixture when brought together, as alcohol and water, or glycerine and water, are said to be *miscible*. Kerosene and water are *non-miscible* liquids.

53. Saturation. — A solution is not a definite compound. A small portion of salt may be dissolved in a large quantity of water; such a solution is said to be *dilute*. In a dilute solution, the substance is as uniformly distributed in all parts of the liquid as it is in one containing a much larger proportion of the dissolved substance. A definite amount of water will dissolve any amount of a given solid up to a fixed quantity. If a liter of water at 20° C. is taken, it is possible to dissolve in it any weight of salt up to 360 grams. When the water has dissolved all the salt it can under given conditions, it is said to be *saturated* with salt at the temperature mentioned. A similar statement can be made concerning the solubility of any solid in any liquid. When any solvent has dissolved all of a given solute that it can, under definite conditions, it is said to be *saturated with respect to that substance under the conditions named*. A solution saturated with one substance may dissolve other substances. Thus, water saturated with respect to salt can dissolve saltpeter.

54. Relation of Solubility to Temperature. — The solubility of most substances is decidedly affected by the temperature. Solids are usually, *but not always*, more soluble in liquids at high than at low temperatures. Sugar, alum, and saltpeter (Fig. 24) are more soluble in hot water than in cold. Salt dissolves nearly as well in cold as in hot water (Fig. 25). Calcium hydroxide, used in the preparation of limewater, is more soluble in cold water than in warm.

Unlike solids, the solubility of gases in liquids decreases

as the temperature rises. Ammonia and carbon dioxide are less soluble in hot water than they are in cold. Different substances differ very much in their solubility in a

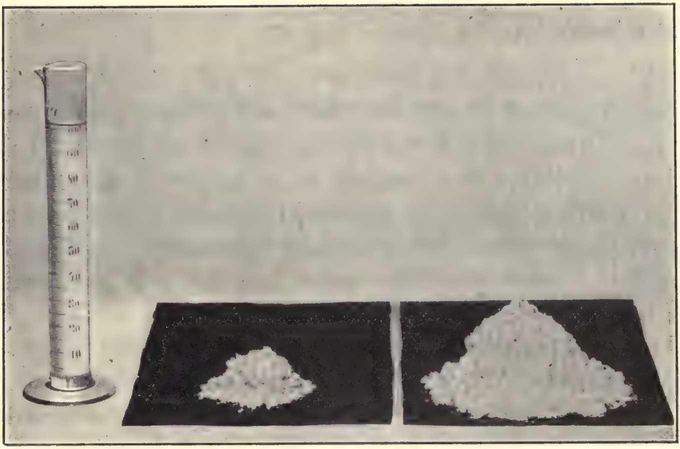


FIG. 24. — RELATIVE SOLUBILITY OF SALTPETER IN COLD AND IN HOT WATER.

given solvent, and different solvents differ in their power to dissolve the same substance.

55. Relation of Solubility to Pressure. — While pressure has little effect on the solubility of solids, it has a decided effect on the solubility of gases. The weight of a gas dissolved in a given volume of a liquid is directly proportional to the pressure.

56. Freezing Mixtures. — There are important energy changes during solution. When a solid is dissolved, energy is absorbed and there is generally a fall in temperature. This is made use of in freezing mixtures. When ice and salt are mixed, some of the ice melts and the salt dissolves in the water. Both processes result in

the absorption of heat, and the temperature of the mixture falls considerably below the freezing point of pure water. When equal parts of ammonium nitrate and

FIG. 25. — RELATIVE SOLUBILITY OF SALT IN COLD AND IN BOILING WATER.

water are mixed, at 0° C., the temperature falls to − 15° C. In the freezing of ice cream, the heat necessary to melt the ice and dissolve the salt is mainly taken from the inner can and its contents.

57. Supersaturation. — If a solution is saturated at a high temperature and then allowed to cool slowly without any disturbance, it will often cool to a lower temperature without depositing any of the substance dissolved (Fig. 26, *a*). But if a particle of the dissolved substance is dropped into the solution, a sudden crystallization takes place, accompanied by an evolution of heat (Fig. 26, *b*, *c*, *d*). Such a solution is said to have been *supersaturated at the lower temperature.* Any disturbance is liable to produce the crystallization.

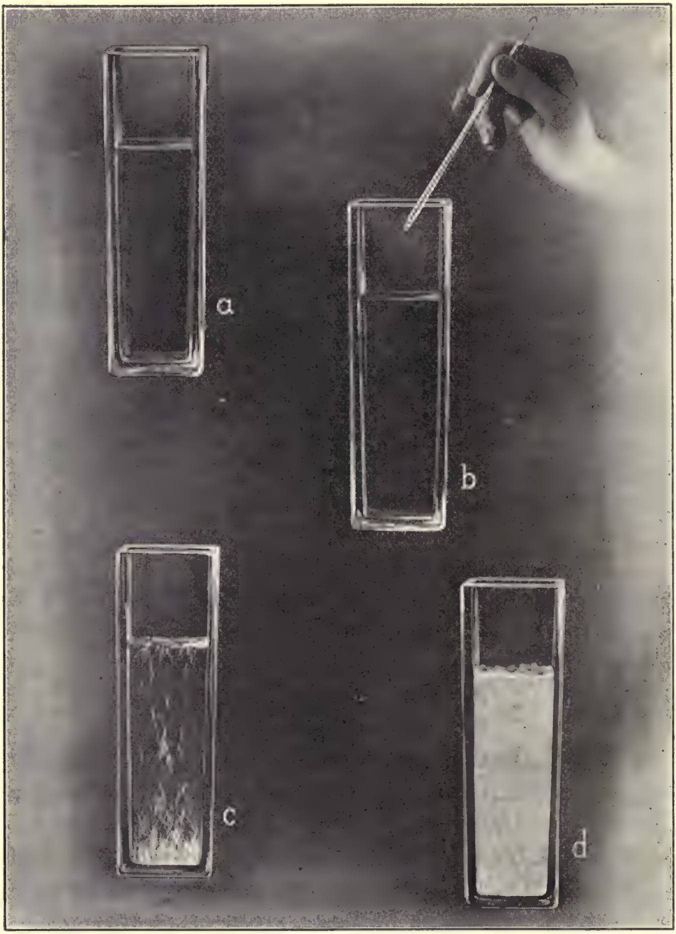


FIG. 26.—CRYSTALLIZATION OF A SUPERSATURATED SOLUTION.

a, clear supersaturated solution; *b*, introduction of a particle of the solute; *c*, crystallization beginning; *d*. crystallization complete.

58. Crystals. — The fact that the solubility varies with the temperature is made use of in separating solids from solution. If a solution that is saturated at a high temperature be allowed to cool slowly, the dissolved substance will often separate into definite forms called *crystals*. Crystals (Fig. 27) are symmetrical and often transparent. Crystals may be obtained from the dilute solution of a solid by the evaporation of the solvent.

59. Water of Crystallization. — Many substances in crystallizing from aqueous solutions unite with a definite quantity of water which is necessary to the shape of the crystal. This water is called *water of crystallization*. Copper sulphate or blue vitriol contains water of crystallization, and if it is heated in a test tube, moisture will be seen on the cooler portions of the tube, and the blue crystal will change to a white powder. The heating has driven off the water of crystallization.

Substances like blue vitriol and crystallized zinc sulphate, formed by the union of a chemical compound with a definite amount of water, are often termed *hydrates*.

60. Efflorescence and Deliquescence. — If a crystal of washing soda is exposed to the air in a dry place, it will lose its water of crystallization and become covered with a fine powder. Such a material is said to be *efflorescent*. An efflorescent substance is one that loses water of crystallization on exposure to the air.

Many materials, as lime, calcium chloride, and caustic potash, usually absorb moisture from the air and are therefore said to be *hygroscopic*. If they absorb sufficient moisture to dissolve them or to cause them to become *wet*, they are said to be *deliquescent*. Such materials are useful as drying agents. Whether a substance will give up its

FIG. 27.—CRYSTALS OF FAMILIAR SUBSTANCES.

a, quartz (ideal); *b*, quartz (actual); *c*, galena or lead sulphide; *d*, garnet; *e*, alum.

moisture to the air or will absorb moisture depends largely on the amount of moisture already in the air and also on the temperature. A hygroscopic substance is one that will absorb moisture from the air. A deliquescent substance is one that absorbs enough to become wet.

HYDROGEN PEROXIDE

Hydrogen and oxygen form a compound other than water in which the weights of hydrogen and oxygen are as 1 to 16. As it contains more oxygen for a given amount of hydrogen than water, it is called hydrogen peroxide or hydrogen dioxide.

61. Preparation. — Hydrogen peroxide is prepared by the action of barium peroxide with dilute acids. Commercially, the barium peroxide is mixed with water to the consistency of cream. This mixture is then added to a dilute solution of sulphuric and phosphoric acids, care being taken to keep the temperature below 15° C.:

$$\begin{matrix}\text{barium} \\ \text{peroxide}\end{matrix} + \text{sulphuric acid} \longrightarrow \begin{matrix}\text{barium} \\ \text{sulphate}\end{matrix} + \begin{matrix}\text{hydrogen} \\ \text{peroxide}\end{matrix}$$

The precipitate of barium sulphate and phosphate is allowed to settle and the solution of hydrogen peroxide decanted, or drawn off.

The commercial form of hydrogen peroxide is its 3% solution. To prevent the peroxide from decomposition, the solution is kept slightly acid or a very small quantity of acetanilid is sometimes added. It is sold under various trade names, such as "Dioxogen" and "Aerozone."

62. Properties. — Hydrogen peroxide itself is a clear, syrupy liquid about $1\frac{1}{2}$ times as dense as water, with which it

is miscible. Pure hydrogen peroxide decomposes with explosive violence. Even in the dilute 3 % water solution, the decomposition proceeds slowly according to the equation:

$$\text{hydrogen peroxide} \longrightarrow \text{water} + \text{nascent oxygen}$$

Nascent oxygen is oxygen at the moment of its liberation from a compound.

63. Uses.—Upon the activity of the nascent oxygen depend the uses of "peroxide" as a bleaching and disinfecting agent. Wool, silk, feathers, hair, and ivory are bleached by the oxidation of their coloring matters. Harmful bacteria and decomposing matter are destroyed by it; hence its use as an antiseptic for superficial wounds and sores. It has very little action on living tissue, and the water formed in its decomposition does not give rise to further irritation, as many other disinfectants do. If acid is present, this may cause irritation. For this reason, it should be mixed with limewater when used as a gargle.

64. Law of Multiple Proportions.—In water the weights of the hydrogen and oxygen are in the ratio of 1 to 8. In hydrogen peroxide the ratio is 1 to 16. Thus the hydrogen in the peroxide is combined with twice as much oxygen as the hydrogen of the water. A similar relation is found in many cases. *Whenever two substances, A and B, unite to form more than one compound, if we consider a fixed weight of A, the weights of B which combine with this fixed weight stand in simple multiple relation to one another.* These ratios may be expressed by small whole numbers. This is known as the *law of multiple proportions* or Dalton's second law. It is a general statement of the fact that we observed (§ 46) when we found

that, if an element has more than one reacting weight, these weights are in a multiple relation.

SUMMARY

Water is the standard for specific gravity and for the specific heat of liquids and solids. Its freezing point and its boiling point are respectively 0° and 100° on the Centigrade thermometer.

Water can be purified by filtration, distillation, and freezing.

A **solution** is a uniform mixture that does not conform to the law of definite proportions.

Water is the most common **solvent**. The amount of a solute in a given quantity of a solvent causes a solution to be either unsaturated, saturated, or supersaturated. Important temperature changes take place during solution.

A **hygroscopic** substance is one that will absorb moisture from the air. If the substance absorbs enough moisture to become wet, it is said to be **deliquescent**.

An **efflorescent** substance is one that loses water of crystallization on exposure to the air.

Water of crystallization is the definite amount of water with which some substances combine when they separate from a solution as crystals.

Hydrogen peroxide can be prepared by the addition of barium peroxide to cold dilute acids, as phosphoric, sulphuric, or hydrochloric. Hydrogen peroxide is a strong oxidizing agent and is used as a germicide and for bleaching.

Hydrogen peroxide consists of 1 part by weight of hydrogen combined with 16 parts by weight of oxygen.

The composition of water and of hydrogen dioxide illustrate the **law of multiple proportions**, which is: Whenever two substances, *A* and *B*, unite to form more than one compound, if we consider

a fixed weight of *A*, the weights of *B* which combine with this fixed weight stand in simple multiple relation to one another.

EXERCISES

1. What physical properties of water determine the fixed points on a Centigrade thermometer?

2. Why does water put out fire?

3. How can salt water be made fit for drinking?

4. How does a solution differ from a chemical compound?

5. What is the chemical statement of the old saying: "Oil and water will not mix"?

6. Distinguish between solvent and solute.

7. Water is saturated with soda at a high temperature and the solution is allowed to cool. Would the solution then be saturated?

8. How could you determine whether a certain solution is saturated, unsaturated, or supersaturated?

9. How could a supersaturated solution of "hypo" be prepared?

10. When sea water is evaporated, why does one of the substances in solution begin to separate before the others?

11. How would you show that any natural water is a dilute solution?

12. Is ammonia more soluble in cold or in hot water?

13. Why does the water from a soda fountain bubble so freely?

14. Why are salt and ice used in ice cream freezers?

15. How could you obtain crystals of washing soda from the dry powder?

16. Distinguish between a hygroscopic and a deliquescent substance. Give an example of each.

17. Why do crystals of washing soda become covered with a coating of white powder when exposed to the air?

18. Why is fused calcium chloride used as a drying agent?

19. There are five oxides of nitrogen in which the weights of oxygen and nitrogen are respectively in the ratios: 16 : 28, 32 : 28, 48 : 28, 64 : 28, and 80 : 28. Show how the composition of these compounds illustrates the law of multiple proportions.

20. Mention three ways by which water can be purified.

21. How does the composition of water illustrate the law of definite proportions?

22. Why does not a solution of hydrogen peroxide keep well when open to the air?

23. If sold at the same price per pound, would it be more economical to buy washing soda before or after it has been exposed to the air for some time?

CHAPTER VII

ATOMS AND MOLECULES

65. Law of Conservation of Mass. — We have studied several substances and some of the laws governing the quantities of matter that take part in chemical actions, without attempting any description of the structure or make-up of the materials used.

Matter is generally defined as anything that takes up room. The different kinds of matter are called *substances.* So far as we know, *matter is indestructible*, nor has any one succeeded in making something from nothing. We may *change its properties*, but we always have the *same amount of matter* after the change as before.

A concise statement of these facts is embodied in the law of the conservation of mass, which may be stated as follows: *The total mass of matter taking part in any chemical process remains unchanged.*

66. Atomic Hypothesis. — We found that the combining or reacting weights are different for various elements but are constant or unchanging for each element. There is apparently something significant in the fact that in the compounds of oxygen with hydrogen the amount of oxygen combined with a given weight of hydrogen is eight, or twice eight, times the weight of the hydrogen.

Since water is composed of eight parts of oxygen and one part of hydrogen, the smallest masses of water must have this composition. For the same reason, the smallest

masses of hydrogen peroxide must contain sixteen parts of oxygen to one of hydrogen. There must be some reason why this number eight is characteristic of oxygen, and why there is no compound of these elements in which the ratio is twelve to one or twenty to one.

John Dalton in 1805 made certain assumptions, known as the *atomic hypothesis*, by which we can readily explain these facts. These assumptions were:

1st, matter is made up of small particles called atoms;

2d, atoms possess the power of attracting or holding on to other atoms;

3d, atoms do not subdivide in taking part in chemical changes;

4th, one atom of an element is exactly like every other atom of that element but differs from an atom of any other element.

67. Atoms. — An atom is the smallest particle of an element that takes part in a chemical change. Different kinds of atoms differ in weight, form, and combining power, but all atoms of the same element must be alike. All the atoms of hydrogen are alike; all the atoms of oxygen are alike.

68. Molecules. — We found that when oxygen and hydrogen combined, a substance was formed which possessed properties differing from either of these elements. The smallest conceivable quantity of water will possess the same characteristic properties as any amount that we can directly observe. The smallest quantity of a substance having the properties of the mass is called a *molecule.* We may assume that each atom of oxygen is accompanied by an atom of hydrogen that always holds on to it. The mass made up of such a pair of minute particles does not

have the properties of hydrogen or of oxygen. It is a new substance — an oxide of hydrogen. Molecules are usually aggregations of atoms. The molecule is the physical unit of the mass, as the atoms comprising it do not separate during *physical* changes.

69. Explanation of the Law of Definite Proportions. — According to the atomic hypothesis, each molecule of water consists of a definite number of atoms of hydrogen in combination with a definite number of atoms of oxygen. Since every atom of the same element has the same weight, the molecule of water must have a definite percentage composition.

Let us assume the mass of the oxygen atom to be 8 times that of the hydrogen atom, and the molecule of water to be composed of 1 atom of oxygen in combination with 1 atom of hydrogen. Then the water molecule would contain 8 parts by weight of oxygen and 1 part by weight of hydrogen, or 88.89% of oxygen and 11.11% of hydrogen. Now a large quantity of water is merely a very great number of molecules and therefore must have the same percentage composition as the single molecule of water. This would explain why it is impossible to make 8.3 grams of oxygen unite with 1 gram of hydrogen. These weights do not contain equal numbers of atoms; the mass of the oxygen will contain the larger number. Consequently, when combination takes place, a number of oxygen atoms would remain unused. The mass of oxygen that has combined would weigh exactly eight times as much as the hydrogen. The 0.3 gram excess of oxygen would remain uncombined.

Whatever the weight of the atoms may be, chemical action *must* take place between definite masses of substances, and the composition of a compound must be

definite. The law of definite proportions, which states that the percentage composition of a chemical compound is constant, is explained by assuming that chemical combinations always take place between atoms.

70. Explanation of the Law of Multiple Proportions. — The law of multiple proportions states that whenever two substances, A and B, unite to form more than one chemical compound, the weights of B that unite with the fixed weight of A are in the ratio of small whole numbers. Now, a fixed weight of A is equivalent to a definite number of atoms of an element. If the hydrogen oxide molecule is composed of one atom of hydrogen and one atom of oxygen, we can imagine combinations of one atom of hydrogen with two, three, or more oxygen atoms. Whatever the combination may be, it is evident from the atomic hypothesis that the weight of oxygen combined with a certain quantity of hydrogen *must* be an integral multiple of the amount which combines with the hydrogen to form hydrogen oxide.

71. Relation of Reacting to Atomic Weights. — The reacting weights are ratios between the weights of different kinds of atoms, or multiples of these weights. If we knew that in water one atom of oxygen was combined with one atom of hydrogen, *as we assumed*, the weight of the oxygen atom would be eight times that of the hydrogen atom. If, however, there are *two* atoms of hydrogen to each oxygen atom, the one atom of oxygen must weigh *sixteen* times as much as one atom of hydrogen. If there are *two oxygen* atoms to each hydrogen atom, each oxygen atom would be *four* times as heavy as the one hydrogen atom.

If we know how many of each kind of atom there are

in a molecule, we can find the relative weights of the atoms. Such determinations have been made by comparison of physical properties.

72. Value of Atomic Hypothesis. — The atomic hypothesis gives a convenient way of explaining the facts upon which the laws of definite and multiple proportions are based. We must not forget, however, that the *laws are statements of facts, based on experimental evidence*, while the atomic hypothesis is used in the attempt to picture a structure or process which would agree with the facts. We do not know that this *is* the way that matter is made up. Perhaps in time a better explanation, based on different suppositions, may be offered, but we do know that it has proved useful in explaining a wide variety of facts and has done more than any other theory for the advancement of chemistry. Practically all scientific explanations of chemical phenomena are based on this hypothesis.

SUMMARY

Matter is anything that takes up room.

Law of Conservation of Mass. — Matter is indestructible. Its properties may be changed, but there is always the same amount of matter after a change as before.

The study of the **weight relations** of chemical changes shows that each element has its definite combining or reacting weight. The amount of any element found in chemical compounds is either this reacting weight or some multiple of it.

These facts are explained by the **atomic hypothesis**. This assumes matter to be made up of small particles which attract or hold on to other particles, but which do not subdivide in chemical changes.

Atoms are the smallest particles of an element that take part in chemical changes. All the atoms of an element are alike and possess the characteristic properties of that element, but differ from the atoms of all other elements. A **molecule** is the smallest quantity of a substance having the properties of the mass.

The **atomic hypothesis** gives a convenient explanation of the facts upon which the laws of definite and multiple proportions are based. It has been the most valuable theory in the establishment of chemistry as a science. Sometime a better explanation may replace this hypothesis.

EXERCISES

1. Why was an extended study of the composition of substances necessary before the atomic hypothesis could be reasonably accepted?

2. Mercury is put into a glass flask which is then sealed, weighed, heated, and weighed again. Why is there no change in the weight, although the mercury turns to a red powder?

3. Why is it that the attempt to make 35.5 grams of chlorine combine with 24 grams of sodium, always leaves 1 gram of sodium uncombined?

4. Dalton knew that one oxide of carbon contained $2\frac{2}{3}$ parts of oxygen to 1 part of carbon and that another oxide was composed of $1\frac{1}{3}$ parts of oxygen to 1 part of carbon. What law do these two facts illustrate? Explain them according to the atomic hypothesis.

5. Sulphur dioxide contains 50 % of sulphur and 50 % of oxygen. Sulphur trioxide contains 40 % of sulphur and 60 % of oxygen. Show how these facts can be used to illustrate the law of Multiple Proportions.

6. Why is the molecule of more importance in physics than in chemistry?

7. Why was not the present atomic hypothesis evolved before the time of Lavoisier?

8. Dalton showed that for one part by weight of hydrogen olefiant gas contained twice as many parts by weight of carbon as marsh gas. Explain these facts according to the atomic hypothesis.

9. Explain this statement: "Without the atomic conception, chemistry would be a chaos of unrelated facts; with the theory, it has become an orderly science" (T. W. Clarke).

10. State the four assumptions of the atomic hypothesis of Dalton.

11. Show how the decomposition of the red oxide of mercury illustrates the law of conservation of mass.

12. Why is a knowledge of reacting weights valuable in the manufacture of synthetic compounds?

CHAPTER VIII

Cl CHLORINE I

73. Chlorine may be said to be a typical non-metallic element. It displays in a marked degree those properties which are regarded as characteristic of the non-metals. The most abundant compound of chlorine found in nature is sodium chloride, common salt. Sodium chloride is a very stable compound; heat does not decompose it except at an extremely high temperature. Chlorine can be obtained from it in several ways.

74. Preparation by Electrolysis. — An electric current can be passed through a solution of common salt, using apparatus similar to that used in the electrolysis of water. The electrodes in this case, however, should be of carbon, since platinum slowly combines with the chlorine that is evolved. The apparatus is filled with a concentrated solution of salt. When the current passes, chlorine is evolved as a gas at the anode and hydrogen at the cathode. Sodium is probably first liberated at the cathode; but since this element reacts rapidly with water, it is impossible for it to accumulate. Hydrogen is set free as a result of the action of sodium with water.

sodium chloride $\longrightarrow$ sodium + chlorine $NaCl \rightarrow Na + Cl$

sodium + water $\longrightarrow$ hydrogen + sodium hydroxide

$2Na + H_2O \rightarrow H_2 + 2NaOH$.

As the final products, we have the two gases, hydrogen and chlorine, and sodium hydroxide which is dissolved in the water.

$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$

75. Preparation by Oxidation of Hydrochloric Acid. — Hydrochloric acid is a solution of a compound of hydrogen and chlorine. The chlorine might be separated by electrolysis, but it is more usual to take advantage of the fact that hydrogen has a great tendency to combine with oxygen; so that if we oxidize hydrochloric acid, the hydrogen will combine with the oxygen to form water, and free chlorine will be obtained. Oxygen from the air may be used. Hydrogen chloride (gas) and air are passed through a heated tube containing a catalytic agent (copper chloride). The action is slow and can be well carried out only on a large scale.

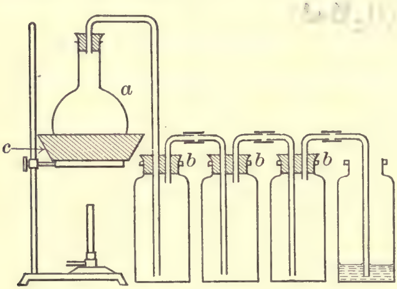


FIG. 28. — PREPARATION OF CHLORINE.
a, generating flask; *b*, bottles for collection of gas; *c*, pan of warm water.

Often on a commercial scale, and in the laboratory, manganese dioxide is the oxidizing agent employed. Concentrated hydrochloric acid solution is mixed with manganese dioxide; when the mixture is warmed, chlorine is evolved (Fig. 28). The hydrogen of the acid combines with the oxygen of the dioxide, forming water. The manganese combines with half the chlorine of the acid, forming manganese chloride, which dissolves in the water the remaining portion of the chlorine is evolved as a gas:

H Cl + Mn O2

4 hydrochloric acid + manganese dioxide ⟶
water + manganese chloride + chlorine

2 H2O + Mn Cl2 + Cl2

The chlorine is not usually collected over water, since dry chlorine is desirable for many experiments and since water dissolves twice its own volume of chlorine at ordinary

temperatures. It is commonly collected by displacement of air, or over salt water, in which it is scarcely soluble. Its density and color render its collection by downward displacement a simple matter.

A mixture of salt, sulphuric acid, and manganese dioxide is often used. The salt and sulphuric acid react and form hydrochloric acid, which is then oxidized by the manganese dioxide.

76. Physical Properties. — Chlorine is a greenish yellow gas, nearly $2\frac{1}{2}$ times as dense as air; it dissolves somewhat in water.

Chlorine has an intensely disagreeable odor, and attacks the membrane of the nasal passages and lungs, producing effects something like those of a bad cold. It is very poisonous; a full breath of the pure gas would probably cause death. Inhaling weak ammonia or alcohol will counteract some of the effects. Chlorine should be prepared and handled with caution to prevent any possibility of inhaling it.

CHEMICAL PROPERTIES

77. Action with Metals. — Chlorine is a very active element. It combines directly with many other elements, especially metals, forming chlorides. When powdered antimony is sprinkled into a jar of chlorine, brilliant sparks are seen and a white cloud of antimony chloride is produced. Arsenic, zinc, copper, and iron, especially when heated, also unite readily with chlorine, with the formation of chlorides:

$$\begin{array}{lll}\text{antimony} & + \text{chlorine} \longrightarrow & \text{antimony chloride} \\ \text{arsenic} & + \text{chlorine} \longrightarrow & \text{arsenic chloride} \\ \text{iron} & + \text{chlorine} \longrightarrow & \text{iron chloride} \\ \text{zinc} & + \text{chlorine} \longrightarrow & \text{zinc chloride}\end{array}$$

These are true cases of combustion, since heat and light appear. So we may say chlorine supports combustion, and thus resembles oxygen.

When molten sodium comes in contact with chlorine, it blazes with a dazzling light, sodium chloride (common salt) being formed. To one who for the first time observes the change, it seems almost incredible that a harmless, household necessity like common salt could result from the union of a gas possessing the disagreeable and poisonous properties of chlorine, with a metal that has sufficient energy to decompose water.

78. Action with Hydrogen. — If a jet of hydrogen is ignited in the air and lowered into a jar of chlorine, a pale, nearly white flame will be produced; the color of the chlorine will disappear, and in the jar we will find a colorless gas, hydrogen chloride, which fumes strongly in moist air. Much heat is given off in the union of chlorine with hydrogen — another similarity between the behavior of chlorine and oxygen. A mixture of chlorine and hydrogen will not combine in the dark; in diffused daylight they combine slowly, and explode when exposed to direct sunlight or other bright light.

The great tendency of chlorine to combine with hydrogen is shown by the fact that it will abstract hydrogen from many compounds. Turpentine is a compound of carbon and hydrogen. If a piece of paper is moistened with warm turpentine and thrown into a jar of chlorine, a violent action occurs, often with the production of a flame, and a heavy deposit of soot (carbon) forms on the side of the bottle. If the breath is blown into the bottle, the moisture will cause the hydrogen chloride there to fume. An action similar to that with the turpentine is seen in the burning of a wax taper in chlorine. Paraffin wax,

like turpentine, contains carbon combined with hydrogen, and only the latter unites with the chlorine.

79. Action with Water. — Although water is a very stable substance, under certain circumstances chlorine will react with it, combining with the hydrogen to form hydrochloric acid and setting the oxygen free. If a tube is filled with a solution of chlorine in water and is allowed to stand in the sunlight, oxygen is slowly formed and collects at the top of the tube (Fig 29):

water + chlorine ⟶ oxygen + hydrochloric acid

The acid formed is dissolved by the water. Chemical actions brought about by the action of light are not uncommon; an important example is the formation of starch in the green leaves of plants under the influence of sunlight. Photographic processes also depend on the effect of light on chemical action.

Chlorine is able to decompose water in the absence of light, provided there is present an oxidizable substance. For this reason chlorine water is a good *oxidizing agent;* the chlorine combines with the hydrogen of the water, and the oxygen set free combines with the other material present.

FIG. 29.

USES

80. Bleaching. — The chief commercial use of chlorine is as a bleaching agent, especially for cotton goods. Cotton fiber is not naturally *white.* If unbleached or colored goods are placed in a jar of chlorine, no action takes place if the cloth is dry; but if moist, many colors are quickly

destroyed (Fig. 30). Some colors are not bleached by chlorine. Many dyes and the coloring-matter of many fibers are easily oxidizable materials; so that when the chlorine acts with the water, forming hydrochloric acid, the oxygen set free changes the coloring-matter to colorless compounds. Chlorine will bleach some colored compounds by decomposing them and combining with the

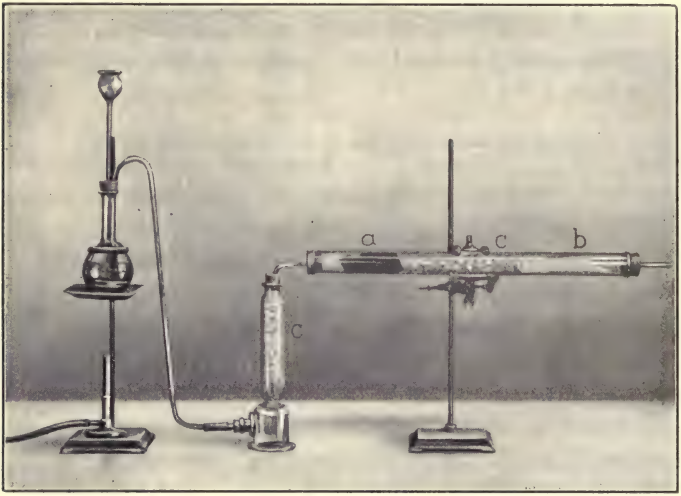


FIG. 30. — BLEACHING WITH CHLORINE.

a, dry colored cloth; *b*, wet cloth; *c*, *c*, calcium chloride to keep moisture from dry cloth.

hydrogen of the dye. Chlorine cannot be used to bleach silk and wool, as it attacks these fibers.

Chlorine is produced in great quantities as a by-product of sodium hydroxide manufacture by the electrolysis of brine. It is sometimes liquefied, in order to transport it easily for use at a distant point. In bleaching, however, chlorine gas is not so generally used as is bleaching-powder, a compound obtained by absorbing chlorine in slaked

lime. The cotton cloth is soaked in a solution of this, and then in dilute acid to liberate the chlorine, and, finally, is thoroughly washed to remove the chemicals (Fig. 31).

In the bleaching action, the destruction of the color was attributed to the oxygen; but oxygen does not ordinarily bleach even weak dyes. It is found that in general elements are more active, that is, have a greater tendency to combine with other substances, if the elements come in contact with the substances at the moment of their liberation from a compound. An element acting under these conditions is said to act in the *născent* (just born) *state*.

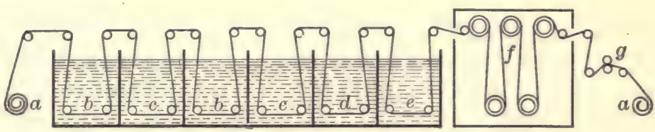


FIG. 31. — DIAGRAMMATIC REPRESENTATION OF BLEACHING.
a, cloth; *b, b*, bleaching powder solutions; *c, c*, acid solutions; *d*, "anti-chlor" (sodium sulphite solution); *e*, water; *f*, drying rolls; *g*, ironing rolls.

81. Disinfecting. — Născent oxygen will readily oxidize and kill microscopic organisms, such as disease germs. Hence chlorine, which sets oxygen free, is a good disinfectant. Bleaching powder (chloride of lime) affords a convenient source of chlorine for this purpose; on standing exposed to air, chlorine is slowly given off. The carbon dioxide of the air unites with water to form a weak acid, which reacts with the bleaching powder, liberating chlorine. The gas can be rapidly liberated by the addition of any common acid to the bleaching powder. Bleaching powder is one of the cheapest and most widely used disinfectants. In recent years, this and other compounds yielding chlorine have come into extensive use for freeing the drinking water for cities and towns from harmful disease germs with which it is contaminated.

SUMMARY

Chlorine occurs in nature combined with metals, the most important compound being salt.

Chlorine is prepared: (1) by electrolysis of brine; (2) by oxidation of hydrochloric acid; (3) by the action of salt with a mixture of manganese dioxide and sulphuric acid. The first and last methods are the more common.

Properties. — Atomic weight, 35.5. Density, 3.2 grams per liter. One volume of water at ordinary temperature dissolves about two volumes of chlorine.

Chlorine is a greenish yellow, poisonous gas characterized by a pungent odor and by its chemical activity. It reacts with metals to form chlorides, and with hydrogen and many hydrogen compounds to form hydrogen chloride. Its reaction with water, yielding nascent oxygen, is utilized in bleaching cotton goods.

The principal **uses** of chlorine are for bleaching, disinfecting, extraction of metals from ores, and the purification of water.

EXERCISES

1. Melted sodium chloride on being electrolyzed gives sodium and chlorine. Why does not the solution yield the same products?

2. In the mixture of salt, sulphuric acid, and manganese dioxide, used in the preparation of chlorine, what is the use of each?

3. If a solution of chlorine is allowed to stand in the sunlight, bubbles collect and the color of the solution fades. Why?

4. Cotton cloth soaked for a long time in chlorine bleaching solution falls to pieces. Why?

5. Chlorine injures wool. What substance, already studied, is used to bleach wool?

6. Describe a case of combustion in which oxygen is not involved.

7. Compare chlorine and oxygen with respect to their chemical activity.

8. When chlorine water is to be used for testing purposes in the laboratory, why should it always be freshly prepared?

9. Explain the action of chlorine on colored cloth when wet.

10. State the methods used for collecting chlorine gas and explain why they are selected.

11. If you accidentally inhaled some chlorine in the laboratory, what means would you employ to counteract its effects?

12. Why are earthenware rather than metal pipes employed to carry chlorine from one part of a bleaching powder factory to another?

13. Give at least two cases in which light produces or hastens chemical action.

14. How is bleaching powder made? State and explain two uses of bleaching powder.

15. What is meant by "nascent oxygen"? Name two substances which depend on nascent oxygen for their disinfecting action.

CHAPTER IX

HYDROCHLORIC ACID

82. Preparation. — One of the most important compounds of chlorine is hydrogen chloride, whose water solution is hydrochloric acid. As its name implies, it may be made by the direct union of hydrogen and chlorine, but the combination is so violent that only small quantities can be made at a time. It may be more conveniently prepared by taking a chloride, *e.g.* sodium chloride, and adding concentrated sulphuric acid (Fig. 32). The action begins immediately and the gaseous hydrogen chloride is evolved so easily that little heating is necessary. Too violent action may be avoided by the successive additions of small quantities of the sulphuric acid to the chloride, using a pan of hot water to heat the mixture. The action may be represented thus:

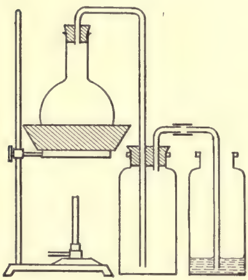


FIG. 32.

sodium chloride + sulphuric acid ⟶

$$\left\{\begin{array}{l}\textbf{sodium}\\ \textbf{chlorine}\end{array}\right. \qquad \left\{\begin{array}{l}\textbf{hydrogen}\\ \textbf{sulphur}\\ \textbf{oxygen}\end{array}\right.$$

sodium sulphate + hydrogen chloride

$$\left\{\begin{array}{l}\textbf{sodium}\\ \textbf{sulphur}\\ \textbf{oxygen}\end{array}\right. \qquad \left\{\begin{array}{l}\textbf{hydrogen}\\ \textbf{chlorine}\end{array}\right.$$

The chlorine of the salt combines with the hydrogen from the sulphuric acid, and the sodium with the other part of the sulphuric acid, that is, with the sulphur and oxygen.

The hydrogen chloride gas may be collected by the downward displacement of the air, or, better, over mercury, since this metal is not attacked by the gas. More frequently, however, the gas is dissolved in water, forming hydrochloric acid, and the acid solution used.

83. General Method for Preparing Acids. — The preparation of hydrochloric acid illustrates a general method for preparing volatile acids. Sulphuric acid is used because it boils (vaporizes) at a comparatively high temperature (338° C.), while hydrochloric acid vaporizes at a much lower temperature. When the sulphuric acid comes in contact with a chloride, a reaction occurs and some hydrochloric acid is formed. The excess of sulphuric acid, the newly formed hydrogen chloride and its solution, hydrochloric acid, are then present in the mixture. The lower boiling hydrochloric acid, however, is soon vaporized, since its boiling point is many degrees below the temperature at which the operation is conducted. The higher boiling sulphuric acid remains behind and gradually completes its reaction with the sodium chloride. Finally, all the hydrochloric acid is driven off and any excess of sulphuric acid remains mixed with the sodium sulphate. Sulphuric acid is generally used in the preparation of other acids.

84. Physical Properties. — Hydrogen chloride is a colorless gas with a sharp, penetrating odor. It is slightly heavier than air. Its solubility in water is most striking, between four and five hundred volumes of the gas dissolving in one volume of water at room temperature.

This solution, commonly known as hydrochloric acid or muriatic acid, contains about 38% by weight of the hydrogen chloride. The high solubility of the gas causes it to unite with the moisture of the air, condensation occurs, and the minute particles of the resulting liquid appear as a white mist or fumes, which can be seen when a concentrated solution of hydrochloric acid is exposed to the air. The fuming is still more marked when the moist breath is blown across the mouth of a tube from which hydrogen chloride gas is issuing.

Hydrogen chloride can be liquefied and also solidified at low temperatures with increased pressure.

85. Chemical Properties. — Neither liquid hydrogen chloride nor the gas, when perfectly dry, shows the chemical properties characteristic of the acids. These properties belong to the water solution. Hydrochloric acid, then, is the aqueous solution of hydrogen chloride. The water solution has a sour taste, changes blue litmus to red, and reacts with many metals, setting free hydrogen and forming a chloride of the metal.

There are four common metals with which hydrochloric acid does not react. These metals are exceptional in their action with acids in general. They are mercury, silver, copper, and lead. Zinc and iron are typical of the metals with which hydrochloric acid does react readily. The equations are:

$$\text{zinc} + \text{hydrochloric acid} \longrightarrow \text{zinc chloride} + \text{hydrogen}$$
$$\text{iron} + \text{hydrochloric acid} \longrightarrow \text{iron chloride} + \text{hydrogen}$$

In these actions the metal replaces the hydrogen in the acid, forming a *chloride*.

86. Typical Properties of Acids. — The compounds commonly known as *acids* are characterized by certain prop-

erties. *Acids are substances that contain hydrogen which may be replaced by metals and whose water solutions turn litmus red.* Substances, such as sugar, whose hydrogen cannot be replaced by metals, are not classed as acids. In general,

$$\text{metal} + \text{acid} \longrightarrow \text{salt of the metal} + \text{hydrogen}$$

When an acid reacts with a metal, hydrogen is liberated and is generally evolved as a gas unless there is an oxidizing agent in the solution, in which case the hydrogen may be oxidized to water. The compound formed by the replacement of the hydrogen of an acid by a metal is called a *salt*. The salt is usually found dissolved in the water that was used to dilute the acid. The portion of an acid molecule remaining after the hydrogen has been removed is called an *acid radical*. *A salt, then, is a metal combined with an acid radical.*

The sour taste of acids is an interesting but not an important distinguishing property. Many fruits owe their sour taste to the presence of acids. Vinegar is hardly more than a dilute solution of acetic acid. The change in color of litmus and of other organic coloring matters is a convenient way of recognizing acids, but is not reliable in all cases.

87. Chlorides. — Hydrochloric acid, like chlorine, reacts with many metals, forming chlorides.

$$\text{metal} + \text{hydrochloric acid} \longrightarrow \text{metallic chloride} + \text{hydrogen}$$
$$\text{metal} + \text{chlorine} \longrightarrow \text{metallic chloride}$$

All the common chlorides are readily soluble in water except three: silver chloride, mercurous chloride, and lead chloride. *The metals having insoluble chlorides do not react with the acid.*

88. Test for a Chloride. — The insolubility of silver chloride is used as a means of identifying soluble chlorides. If a solution of silver nitrate is added to a solution of a chloride, a white, curdy solid separates; this precipitate darkens in the light. By a *precipitate* we mean a solid resulting from a chemical action in solution, that separates because it is insoluble.

$$\text{chloride of a metal} + \text{silver nitrate} \longrightarrow \\ \text{nitrate of the metal} + \text{silver chloride}$$

Addition of silver nitrate causes a white precipitate in many other solutions, but *silver chloride is insoluble in dilute nitric acid.* As hydrochloric acid is a solution of *hydrogen chloride*, the same test *together with the litmus test* serves to identify it.

89. Uses of Hydrochloric Acid. — Very small quantities of hydrochloric acid are found in the gastric juice and are necessary in the gastric digestion. It is often given as a medicine in certain cases of indigestion. Large quantities of hydrochloric acid are employed in the preparation of chlorine to be used in the manufacture of bleaching powder. It is also used in the making of chlorides, in cleaning metals, and in the manufacture of glue and gelatine.

90. Proportion of Hydrogen in Hydrogen Chloride. — When sodium is placed in hydrogen chloride, a violent reaction occurs, during which the sodium replaces the hydrogen. The reaction can be made less energetic by using sodium amalgam instead of sodium. Sodium chloride, mercury, and hydrogen result from the reaction. The volume of the hydrogen remaining after the reaction is found to be one half that of the hydrogen chloride taken.

The experiment can be performed in the following man-

ner: hydrogen chloride is generated by causing sulphuric acid to drop *slowly* into concentrated hydrochloric acid (Fig. 33, *A*). As a result of the action of the sulphuric acid with the water, gaseous hydrogen chloride is evolved. It is then dried by being made to pass through concentrated sulphuric acid. A glass tube, about 70 cm. long and 1.5 cm. in diameter, is filled with the dry hydrogen chloride by the displacement of mercury.

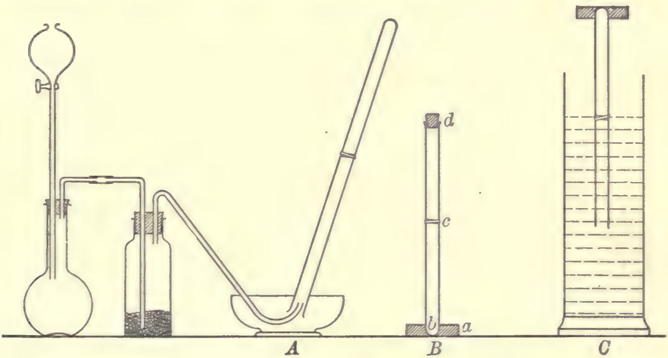


FIG. 33. — VOLUME COMPOSITION OF HYDROGEN CHLORIDE.
a, cork to prevent heating tube while handling; *b*, sodium amalgam; *c*, rubber band; *d*, rubber stopper.

Sodium amalgam is dropped into the tube of hydrogen chloride and the mouth of the tube instantly closed with a stopper (Fig. 33, *B*). The tube is then inverted several times in succession, its mouth placed under some water in a tall cylinder, and the stopper removed (Fig. 33, *C*). Water rushes into the tube.

The remaining gas (hydrogen) is brought under atmospheric pressure by raising or lowering the tube in the cylinder until the liquid on the inside of the tube is at the same level as that outside. A small rubber band is then placed on the tube at the surface of the liquid.

The volume occupied by the hydrogen is then found by measurement to be one half that occupied by the hydrogen chloride. This gives no data in regard to the volume occupied by the chlorine.

91. Relative Composition of Hydrogen Chloride. — The composition by volume can be shown by the use of the electrolysis apparatus shown in Fig. 34. Hydrochloric acid, having a specific gravity of 1.1, is placed in the tubes ***a***. The three-way stopcocks *b* are turned so that there is a passage from *c* to *d* and a saturated solution of sodium chloride is drawn from the dishes *i* into the collecting tubes *e* until they are filled. The stopcocks are then turned so that there is a passage from *f* to *d*. The current is turned on, and as soon as the hydrochloric acid above the anode is saturated with chlorine, the stopcocks are turned so that the hydrogen and chlorine will pass into the collecting tubes *e*. When the upper surfaces of the sodium chloride solution are just above the support *g*, it is inclined, if need be, so as to mark the relative height of the solution in the collecting tubes. The lower support *h* is then made parallel with *g*. The solutions in *ee* between *g* and *h* are displaced in the same time, showing that equal

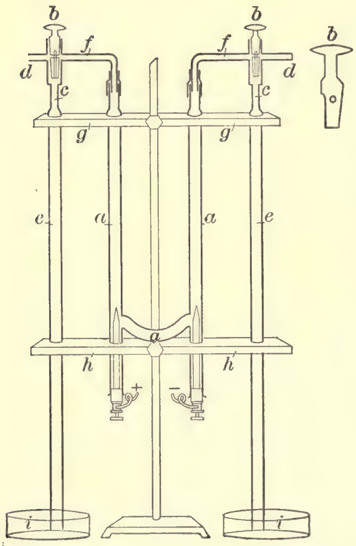


FIG. 34. — ELECTROLYSIS OF HYDROCHLORIC ACID.

volumes of hydrogen and chlorine are obtained by the electrolysis of hydrochloric acid.

92. Volumetric Composition of Hydrogen Chloride. — In the electrolysis of hydrogen chloride solution just described, we have shown that the volume of the hydrogen set free is equal to the volume of the chlorine. By the sodium-amalgam method, the volume of the hydrogen chloride was found to be twice the volume of the hydrogen. Hence we may represent the volumetric composition of hydrogen chloride by the equation:

$$\text{1 volume of hydrogen} + \text{1 volume of chlorine} \longrightarrow \text{2 volumes of hydrogen chloride}$$

SUMMARY

Hydrogen chloride may be prepared: (1) by direct union of its elements; (2) by the action of sulphuric acid with a chloride. The latter is the common method.

It is a **gas** with a pungent odor. One liter under standard conditions weighs 1.64 grams. One liter of water at 20° dissolves 450 liters of hydrogen chloride.

The dry gas is inactive; its water solution is a typical acid. The replacement of the hydrogen by a metal gives a chloride. All but three of the common chlorides are soluble in water.

Acids contain hydrogen that can be replaced by a metal. Their water solutions turn litmus red and usually have a sour taste.

Two liters of hydrogen chloride, when decomposed, yield one liter of hydrogen and one liter of chlorine.

The chief **uses** of hydrochloric acid are for the preparation of chlorine and chlorides, and for cleansing metals.

EXERCISES

1. Why is not the direct union of hydrogen and chlorine a convenient method of making hydrogen chloride?

2. Should hydrogen chloride be collected by upward or downward displacement?

3. Give a reason for the use of each substance employed in the preparation of hydrogen chloride.

4. State and explain the general method for preparing volatile acids.

5. Why is tin moistened with a solution containing hydrochloric acid before being soldered?

6. When chlorine is brought in contact with ammonia, which is a compound of hydrogen and nitrogen, a reaction occurs. Name one compound formed.

7. What products are formed when metallic magnesium is treated with hydrochloric acid?

8. What is formed when an amalgam of potassium and mercury is exposed to hydrogen chloride?

9. How would you determine whether or not a gas is hydrogen chloride?

10. State the difference between hydrogen chloride and hydrochloric acid.

11. Name two metals that replace hydrogen in dilute hydrochloric acid and two that do not.

12. Give three distinct characteristics of acids in water solution.

13. State the properties that cause hydrochloric acid to be called a typical acid.

14. What is a salt? A chloride? An acid?

15. How could you determine whether an unknown substance were a chloride? Whether it were hydrochloric acid?

16. Give the volume composition of hydrogen chloride and state how it is determined.

CHAPTER X

MOLECULAR COMPOSITION

93. Volume Relation of Gases. — It has been shown in the volumetric synthesis of steam (§ 42) that

1 volume of oxygen with 2 volumes of hydrogen gives 2 volumes of steam.

1 volume of chlorine with 1 volume of hydrogen gives 2 volumes of hydrogen chloride (§ 92).

The study of the actions of other gases gives similar results; thus:

1 volume of nitrogen with 3 volumes of hydrogen gives 2 volumes of ammonia.

In these cases the ratio of the volumes of the gases that combine may be expressed in whole numbers; this is also true of the ratio of the volume of each of the combining gases to the volume of the product.

94. Law of Gay-Lussac. — The relations stated in § 93 were first generalized by Gay-Lussac in his law of volumes: *The relative combining volumes of gases and the volume of the product, if gaseous, may be expressed by small whole numbers.* Two other generalizations relative to gases are:

II Boyle's Law: the volume of any gas varies inversely as the pressure, if the temperature remains the same; and

I Charles' Law: the volume of any gas varies directly as the absolute temperature, if the pressure remains the same.

95. Reacting Weights and Volume Weights of Gases. — We found that a volume of chlorine weighs 35.5 times as much as an equal volume of hydrogen, if the comparison is made under similar conditions of temperature and pressure. Similarly we found that oxygen weighs 16 times as much as hydrogen. The weights of equal volumes of oxygen and chlorine are, then, as 16 to 35.5. It will be noticed that these numbers are reacting weights of the elements. A similar regularity is found in the case of other gaseous elements. Hence we make the general statement that *the ratio of the weights of equal volumes of gaseous elements is the same as the ratio of certain of their reacting weights.*

96. Avogadro's Hypothesis. — These four uniformities in the behavior of gases led Avogadro in 1811 to make the following hypothesis: *Equal volumes of gases under like conditions of temperature and pressure contain the same number of molecules.* That is to say, a liter of hydrogen contains just *as many molecules* as a liter of oxygen, a liter of chlorine, a liter of hydrogen chloride, or a liter of any other gas measured under the same conditions of temperature and pressure.

The actual number of molecules in the liter of any gas is very great, but we have no concern with the actual number. We know nothing whatever of the number of molecules in equal volumes of solids or of liquids.

97. Number of Atoms in the Molecules of Gaseous Elements. — In a former chapter (cf. § 71) we showed that if we knew the number of atoms of each element in a molecule, we could determine the relative weight of the atoms. We cannot count the number of atoms in a molecule, but by means of Avogadro's hypothesis we can arrive at a definite *belief* in the matter.

Experiment shows that *one* volume of chlorine and *one* volume of hydrogen combine to form *two* volumes of hydrogen chloride.

1 volume of hydrogen + 1 volume of chlorine
$\longrightarrow$ 2 volumes of hydrogen chloride

Suppose the given volume of hydrogen contains 1000 molecules, then by Avogadro's hypothesis, 1000 molecules must also be contained in an equal volume of chlorine; and likewise, since the hydrogen chloride occupies *twice* the space of the hydrogen, the volume of hydrogen chloride resulting from the combination must contain 2000 molecules. Or, briefly stated:

1000 molecules of hydrogen + 1000 molecules of
chlorine $\longrightarrow$ 2000 molecules of hydrogen chloride

In each of these 2000 molecules of hydrogen chloride there must be some hydrogen, at least *one* atom (cf. § 68). At least 2000 atoms of hydrogen have, therefore, been obtained from the 1000 molecules of hydrogen. In other words, the experiment indicates that each hydrogen molecule splits into *at least* two parts during the chemical action. These parts cannot be smaller than atoms, since atoms are indivisible. Consequently, each hydrogen molecule contains *at least two* atoms of hydrogen. Similar reasoning shows that the *chlorine molecule* also contains at least *two atoms.*

It is to be noted that *any even number* might be used instead of two, but since there is no chemical action known in which either the hydrogen or the chlorine molecule seems to divide into more than two parts, it is not probable that there are more than two atoms in either of these molecules.

Let us consider the composition of steam. Experiment

shows that *two* volumes of hydrogen with *one* volume of oxygen yield *two* volumes of steam. Assuming 1000 molecules to a volume, and reasoning according to Avogadro's hypothesis, the two volumes of hydrogen and of steam must each contain 2000 molecules. Then:

$$2000 \text{ molecules of hydrogen} + 1000 \text{ molecules of oxygen} \longrightarrow 2000 \text{ molecules of steam}$$

In each of these 2000 molecules of steam, there must be *at least one* atom of oxygen.

Not less than 2000 atoms of oxygen have, therefore, been obtained from the 1000 molecules of oxygen. Consequently, each oxygen molecule contains *at least two atoms* of oxygen. It has been already shown that the hydrogen molecule contains at least two atoms. The steam molecule, then, must contain at least one oxygen atom and two hydrogen atoms.

While the molecules of all the common gaseous elements contain two atoms, this is not true of all elements in the gaseous state. For example, mercury and zinc have each one atom to the molecule; phosphorus has four; and sulphur eight, six, or two, according to the temperature.

SUMMARY

Uniformities in the Behavior of All Gases:

Boyle's Law: The volume of any gas varies inversely as the pressure if the temperature remains the same.

Charles' Law: The volume of any gas varies directly as the absolute temperature if the pressure remains the same.

Gay-Lussac's Law: The relative combining volumes of gases and the volume of the product, if gaseous, may be expressed by small whole numbers.

The weights of equal volumes of gaseous elements are to each other as certain of their reacting weights.

The **uniformities in the behavior** of all gases, independent of their chemical composition, leads to the belief that **equal volumes of gases, under the same conditions of temperature and pressure, contain the same number of molecules.** (Avogadro's Hypothesis.)

It follows from Avogadro's hypothesis, and from the volumetric composition of gaseous compounds, that the elements hydrogen, oxygen, chlorine, and nitrogen each have **two** atoms to the molecule. Zinc and mercury have **one** atom to the molecule; phosphorus and arsenic have **four.**

EXERCISES

1. What uniformities (laws) are known about the physical and chemical behavior of gases?

2. What are the evidences in support of Avogadro's hypothesis?

3. Show how Gay-Lussac's Law of Volumes applies to the union of hydrogen and chlorine.

4. Show by Gay-Lussac's Law that there always must be some oxygen left when you attempt to combine three volumes of hydrogen with an equal volume of oxygen.

5. One liter of marsh gas in burning combines with two liters of oxygen. How many molecules of oxygen are needed to react with one molecule of marsh gas?

6. Approximately what are the relative numbers of molecules of oxygen and nitrogen in air?

7. What volume of *air* is needed for the complete combustion of 100 c.c. of marsh gas?

8. Two molecules of nitric oxide (gas) unite with one molecule of oxygen when the two are brought together. How many cubic centimeters of oxygen would be needed for complete re-

action with 64 c.c. of nitric oxide? How much air would be needed for the same purpose? 32 + 5 =

9. Give reasons for believing that the oxygen molecule contains at least two atoms.

10. One volume of hydrogen unites with one volume of bromine gas, forming two volumes of hydrogen bromide. How many atoms are there in the molecule of gaseous bromine? Explain.

11. Two tanks of equal capacity contain oxygen. The gas in the first is under atmospheric pressure; that in the second is under 3.2 atmospheres' pressure. How does the weight of oxygen in the second tank compare with the weight of that in the first?

12. When two volumes of hydrogen chloride are decomposed by sodium amalgam, they yield one volume of hydrogen. Assuming 3000 molecules to one volume, show how Avogadro's hypothesis can be used to prove the composition of the hydrogen molecule.

13. Why is the principle of Avogadro a hypothesis rather than a law?

CHAPTER XI

ATOMIC AND MOLECULAR WEIGHTS

98. Atomic Weights. — Since it has been shown that there are twice as many hydrogen atoms as oxygen atoms in the molecule of steam, the weight of the oxygen atom relative to the weight of the hydrogen atom can now be determined. The oxygen in water weighs eight times as much as the hydrogen. The weight of the *hydrogen atom* is taken as the unit in comparing the weights of the atoms of different elements[1]; therefore, the *two* hydrogen atoms contained in a molecule of water must have a weight of 2. The one oxygen atom combined with the two hydrogen atoms must weigh 8×2, or 16. The atomic weight of hydrogen is 1; of oxygen, 16. *The atomic weight of an element is a number which expresses how many times its atom is as heavy as the hydrogen atom.* It corresponds to one of the reacting weights.

99. Density and Specific Gravity. — By the density of a substance is meant the number of units of mass that occupy a unit volume. In scientific work the gram is the unit of mass, and the cubic centimeter the unit of volume. The density of a substance, then, is the number of grams of that substance occupying one cubic centimeter. One gram of water at 4° C. occupies one cubic centimeter.

[1] In tables of exact atomic weight in common use, the standard actually taken is oxygen = 16.00. This makes the atomic weight of hydrogen slightly greater than 1. For ordinary purposes, however, the hydrogen standard of 1 is satisfactory.

The *specific gravity* of a substance is the weight of that substance divided by the weight of an equal volume of some substance taken as a standard. Water is taken as the standard of specific gravity for liquids and solids. The term *density* is often used incorrectly for specific gravity.

100. Specific Gravity and Vapor Density of Gases. — There are two standards for the specific gravity of gases, air and hydrogen. For experimental purposes air is commonly used; for purposes of calculation hydrogen is more convenient. The term *specific gravity* of a gas, when used without explanation, means the number of times the gas is as heavy as an equal volume of air. The term *vapor density* means the specific gravity of a gas with respect to hydrogen. *Vapor density is the number of times a gas is as heavy as an equal volume of hydrogen.* The vapor density of a gas is found by determining the weight of a liter of the gas and comparing this weight with the weight of a liter of hydrogen under the same conditions of temperature and pressure. Such comparisons of the weights of equal volumes of gases can be made at any convenient temperature and pressure. The usual custom, however, is to compare weights of equal volumes at 0° C. and 760 mm.; that is, at standard conditions. In the determination of specific gravity, great care must be taken to have the gases pure and dry.

101. Determination of Molecular Weights. — *The molecular weight of a substance is a number which expresses how many times its molecule is as heavy as the hydrogen atom.*

It follows from Avogadro's hypothesis that the weights of equal volumes of two gases will have the same ratio as the weights of their molecules. This can be shown by the following reasoning. One liter of hydrogen, measured

Theodore W. Richards was born in Germantown, Pennsylvania. He is now Erving Professor of Chemistry in Harvard University. His revisions of the atomic weights of more than a score of elements have been accorded world-wide recognition. His later researches have dealt with atomic volumes, electrochemical and thermochemical behavior of the elements, and compressibility of the atoms.

Edward W. Morley was born in 1838 at Newark, New Jersey. He graduated at Williams and in 1869 became Professor of Chemistry in Western Reserve University.

He has explored fields in both physics and chemistry. His greatest achievement was the determination of the exact ratio by which oxygen and hydrogen combine by weight, as this ratio has been generally accepted.

under standard conditions, weighs 0.09 gram; one liter of oxygen, measured under similar conditions, weighs 1.43 grams. The liter of oxygen is $\frac{1.43}{0.09}$, or almost 16 times as heavy as a liter of hydrogen. If there are *n* molecules in a liter of oxygen, there must be, according to Avogadro's hypothesis, *n* molecules in a liter of hydrogen. Since *n* molecules of oxygen weigh 16 times as much as *n* molecules of hydrogen, one molecule of oxygen must weigh 16 times as much as one molecule of hydrogen.

The hydrogen molecule we showed to contain two atoms, hence its molecular weight is 2. The molecular weight of oxygen is, therefore, 16×2, or 32. Thus we see that the *molecular weight of a gas must be twice its vapor density.* As chlorine is 35.5 as dense as hydrogen, its molecule weighs 71 times as much as an atom of hydrogen. We have proved that the chlorine molecule contains two atoms, so the atom of chlorine weighs 35.5 times as much as an atom of hydrogen.

FIG. 35. — GRAM-MOLECULAR VOLUME.

102. Alternative Method for Determination of Molecular Weights.[1] — A gram-molecular weight of a gas is as many grams of that gas as there are units in its molecular weight. The molecular weight of hydrogen is 2. Two grams is a gram-molecular weight of

[1] The instructor is advised to have the class omit either paragraph 101 or paragraph 102. The use of both methods may confuse beginners.

hydrogen. Since one liter of hydrogen weighs, under standard conditions, 0.09 gram, two grams of hydrogen will occupy $2 \div 0.09$, or 22.2 *liters* (Fig. 35).

The gram-molecular weight of *any* gas occupies this same volume. This is shown by the following considerations. A gram-molecular weight of a gas equals 2 grams multiplied by the vapor density (V. D.) of the gas (§ 100). Since the vapor density of a gas is the number of times that gas is as heavy as an equal volume of hydrogen, the weight of 1 liter of any gas is equal to the weight of 1 liter of hydrogen (.09 g.) multiplied by the vapor density of the gas. Now, 2 grams of hydrogen occupies 22.2 liters at standard conditions $\left(\frac{2}{.09} = 22.2\right)$, and, according to the statements just made, the relations shown by the following equalities will also hold :

$$\frac{\text{gram-molecular weight of any gas}}{\text{weight of 1 liter of that gas}} = \frac{2\text{ g.} \times \text{V. D.}}{.09\text{ g.} \times \text{V. D.}} = \frac{2\text{ g.}}{.09\text{ g.}}$$
$$= 22.2 \text{ liters}$$

Therefore, a gram-molecular weight of *any* gas occupies a volume of 22.2 liters.

2 grams of hydrogen have a volume of 22.2 liters.
32 grams of oxygen have a volume of 22.2 liters.
71 grams of chlorine have a volume of 22.2 liters.
36.5 grams of hydrogen chloride have a volume of 22.2 liters.

Therefore, 32, 71, and 36.5 are respectively the molecular weights of oxygen, chlorine, and hydrogen chloride.

If 82 c.c. (0.082 liter) of carbon dioxide weigh 0.1623 gram, we can find the weight of 22.2 liters by the proportion :

$$0.082 \text{ liter} : 22.2 \text{ liters} :: 0.1623 \text{ gram} : x \text{ gram}$$
$$x = 44 \text{ grams}$$

Therefore, the weight of the carbon dioxide molecule is 44. It is 44 times as heavy as the hydrogen *atom*.

103. Determination of the Number of Atoms in the Molecule of a Compound. — We have shown how the number of atoms in a molecule of a gaseous element is determined in the cases of hydrogen, oxygen, and chlorine (cf. § 97). When the gas is a compound, we can find how many of each kind of atoms are present by ascertaining

(*a*) the composition by weight;
(*b*) the molecular weight.

In the case of carbon dioxide:

(*a*) its composition by weight is 27.3 % carbon, 72.7 % oxygen;
(*b*) its molecular weight is 44, as shown above.

The weight of the oxygen in the molecule is 72.7 % of 44, or 32. We have shown that the *atomic weight* of oxygen is 16, so there must be two atoms of oxygen in each molecule of carbon dioxide.

The carbon in each molecule will be 27.3 % of 44, or 12. Carbon cannot be vaporized, consequently we cannot determine its atomic weight by the method used for oxygen. However, many compounds of carbon are gases, and *in no case* does the carbon furnish less than twelve parts of the molecular weight. That is, the smallest portion of carbon that enters into chemical combination (*the atom*) weighs twelve times as much as the hydrogen atom.

The carbon dioxide molecule is composed, therefore, as its name indicates, of *one* atom of carbon (weighing 12) and *two* atoms of oxygen.

SUMMARY

It follows from Avogadro's hypothesis that the **vapor densities** of gases are in the same ratio as their molecular weights.

The **molecular weight of a gas** can be calculated by multiplying the molecular weight of hydrogen, 2, by the vapor density of the gas. The vapor density of a gas is determined experimentally.

The molecular weight of a gas can also be determined by making use of the fact that the gram-molecular weights of all gases have the same volume, 22.4 liters. Knowing the weight of any given volume of the gas, the required molecular weight can be found from a proportion in which the weight and volume and the number 22.4 are the three known quantities.

The molecular weight of hydrogen is 2, of oxygen 32, of chlorine 71, of nitrogen 28.

PROBLEMS

1. A liter of bromine gas, at standard conditions, would weigh 7.2 grams. What is its vapor density? Using the answer to question 10, Chapter X, determine the atomic weight of bromine.

2. A liter of marsh gas, at standard conditions, weighs 0.72 gram. What is the molecular weight of marsh gas?

3. Methane gas is composed of carbon 75 %, hydrogen 25 %, and its molecular weight is 16. What part of the molecular weight of the compound is carbon? What part is hydrogen? The atomic weight of carbon is 12; how many atoms of each element are there in a molecule of the compound? CH_4

4. 0.58 gram of acetylene gas has a volume of 495.7 c.c., standard conditions. What is the vapor density of acetylene? What is its molecular weight? [illegible]

5. Determine the molecular weight of the following substances:

Gas	Weight Data
Nitrous oxide	290 c.c. weighs 0.574 g.
Hydriodic acid	93 c.c. weighs 0.531 g.
Ether (gaseous conditions)	230 c.c. weighs 0.766 g.

6. Air is 14.44 times as heavy as hydrogen. Compute the specific gravity of the gases mentioned in the above problems.

7. What is the numerical ratio between the molecular weight of a gas and its vapor density? What is the ratio between the molecular weight and the specific gravity?

8. Determine the molecular weights of the following gases:

Gas	Sp. G. (air)
Ammonia	0.597
Carbon monoxide	0.968
Cyanogen	1.806

9. 50 c.c. of a certain gas at standard conditions weighs 0.076 gram. What is its molecular weight?

10. Compute the molecular weight of nitrogen from the following data: 222.5 c.c. of nitrogen at 27° C. and 730 mm. pressure, weighs 0.25 gram.

11. If 540.1 c.c. of a certain gas, when measured dry at 18° C. and 750 mm. pressure, weighs 1.71 grams, what is the molecular weight of the gas?

CHAPTER XII

CHEMICAL FORMULAS AND NAMES

104. It is a great convenience to have a short, accurate method of representing the chemical changes taking place in a chemical action. We have been expressing those changes in the form of equations, in which we have on one side the names of the substances which enter into the action, and on the other the names of the products formed. According to the atomic theory, chemical action takes place between molecules, by the rearrangement and redistribution of the atoms. If we express the action in terms of molecules and atoms, it becomes much more significant. Symbols and equations are used to represent chemical actions as simply as possible.

105. Significance of the Symbol. — The symbol of an element is usually the initial letter of the name capitalized. Thus *one atom* of hydrogen is represented by a capital H, and as the atom has mass, this H represents also a *definite mass* of hydrogen, *one part by weight.* The symbol thus means not only the substance, but a definite quantity of the substance. O means one atom of oxygen, *also* sixteen parts by weight of oxygen.

When several substances have the same initial, another letter conspicuous in the name is added, but not capitalized, as C (carbon); Ca (calcium); Cd (cadmium); Cl (chlorine). In some cases the symbol is derived from a Latin name, as Fe (*ferrum*, iron); Cu (*cuprum*, copper); Na (*natrium*, sodium); and K (*kalium*, potassium).

106. Significance of the Formula. — The formula of a molecule is formed by grouping together the symbols of the atoms composing it. The molecule of hydrogen chloride was found to consist of one atom of hydrogen and one atom of chlorine. Its formula, therefore, is HCl. This means

(1) one molecule of hydrogen chloride;
(2) that the molecule of hydrogen chloride contains one atom of hydrogen and one atom of chlorine;
(3) that one molecule of hydrogen chloride is composed of 1 part by weight of hydrogen and 35.5 parts by weight of chlorine;
(4) 36.5 parts of hydrogen chloride by weight;
(5) 1 part by volume of hydrogen chloride (Avogadro's hypothesis).

When a molecule contains more than one atom of the same kind, the symbol is not usually repeated, but the number of the atoms is written as a subscript to the symbol. The formula of water is usually written H_2O and not HOH. As stated above, H_2O means

(1) one molecule of water;
(2) that one molecule of water is composed of two atoms of hydrogen and one atom of oxygen;
(3) that one molecule of water is composed of 2 parts by weight of hydrogen and 16 parts by weight of oxygen;
(4) 18 parts by weight of water;
(5) 1 part by volume of steam.

It is only when the compound is in a gaseous state that its formula represents one part by volume. Thus, NaCl represents one molecule of sodium chloride as composed of

one atom of sodium and one atom of chlorine; that is, 23 parts by weight sodium and 35.5 parts chlorine, or a total weight of 58.5 sodium chloride. It also represents one volume of the *gaseous salt*, but *not* of the *solid salt*.

107. The Number of Molecules that take part in a reaction is represented by means of a coefficient.

$2\ HCl$ = 2 molecules hydrochloric acid
$3\ H_2O$ = 3 molecules water

CALCULATION OF THE FORMULA

108. Method when Vapor Density is Known. — If we know the vapor density, the composition and the atomic weights, we can calculate the molecular weight and the formula.

Example:

The vapor of alcohol is 23 times as heavy as hydrogen. The composition of alcohol is: carbon, 52.17 %; hydrogen, 13.04 %; oxygen, 34.78 %; the atomic weights are 12, 1, and 16 respectively. Required to calculate the formula.

Solution:

Since the vapor density referred to hydrogen is 23, the molecular weight must be 46 (cf. § 101). The weight of carbon in the molecule is 52.17 % of 46, or 24. The weight of the hydrogen in the molecule is 13.04 % of 46, or 6. The oxygen is 34.78 % of 46, or 16,

Since one atom of carbon weighs 12, there must be two carbon atoms to make up the 24 parts of carbon in the alcohol molecule. There must be six hydrogen atoms, as each weighs 1, and as an oxygen atom weighs 16, there can

be but one of these atoms in the molecule of alcohol. The formula for the alcohol is therefore C_2H_6O.

The vapor density of acetylene is 13; its composition is carbon, 92.3 %; hydrogen, 7.7 %. What is its formula?

Solution:

Since the vapor density is 13, the molecular weight is 26.

	Percentage composition	Weight of element in molecule	Atomic weight	Number of atoms
carbon	92.3	24	12	2
hydrogen	7.7	2	1	2

Hence the formula is C_2H_2.

This method can be used only when the molecular weight can be determined by experimental means.

109. Method when Molecular Weight is not Known. — Since the oxygen atom weighs 16 times as much as the hydrogen atom, there are $\frac{1}{16}$ as many atoms in 1 gram of oxygen as there are in 1 gram of hydrogen. The relative numbers of atoms per gram of several elements may be calculated by dividing 1 gram by the atomic weight of each of the elements in question. Likewise it is true that if we divide *any* given weights of elements by their respective atomic weights, we obtain numbers that are in the *ratio* of the numbers of atoms present.

The percentage composition of sulphuric acid is:

hydrogen	2.04 %
sulphur	32.65 %
oxygen	65.31 %

This means that 100 parts by weight of sulphuric acid contain

2.04 parts by weight of hydrogen,
32.65 parts by weight of sulphur, and
65.31 parts by weight of oxygen.

If we divide the parts by weight of each of these elements respectively by its atomic weight, we obtain the *relative* number of atoms in the molecule of the compound.

hydrogen	$2.04 \div 1 = 2.04$
sulphur	$32.65 \div 32 = 1.02$
oxygen	$65.31 \div 16 = 4.08$

For every 2.04 atoms of hydrogen it contains, sulphuric acid must contain 1.02 atoms of sulphur and 4.08 atoms of oxygen. But, since not less than 1 atom of an element can enter a molecule of a compound, the ratio $2.04:1.02:4.08$ must be reduced to the smallest possible whole numbers, if we are to write the simplest chemical formula that will correspond to the percentage composition of sulphuric acid. These whole numbers may be found by dividing each term of the ratio by the smallest term.

$$2.04 \div 1.02 = 2 \text{ hydrogen}$$
$$1.02 \div 1.02 = 1 \text{ sulphur}$$
$$4.08 \div 1.02 = 4 \text{ oxygen}$$

H_2SO_4 is, therefore, the simplest formula that can be used to represent the chemical composition of sulphuric acid In many cases it is impossible to determine the molecular weight by vapor density or other experimental methods. In these cases the simplest (or *empirical*) formula that agrees with the percentage composition is the one that is accepted. The true formula for sulphuric acid is either H_2SO_4 or some multiple of H_2SO_4. Since this formula corresponds to the molecular weight of sulphuric acid, that is indicated by the osmotic pressure (§ 143) of its solutions, and since its general behavior indicates that it contains but 2 hydrogen atoms, H_2SO_4 is believed to be the correct formula.

The formula for benzol may be calculated as follows:

Percentage composition		Atomic weight	Atomic ratio	Simplest atomic ratio	Simplest formula		Corresponding molecular weight
carbon	92.3 %	12	7.7	1	C	or CH	12
hydrogen	7.7 %	1	7.7	1	H		1
							13

But, since the vapor density of benzol has been found by experiment to be 39, the molecular weight of benzol must be 2×39, or 78. Now 78 is six times 13, the molecular weight corresponding to the formula CH. The true formula for benzol is, therefore, C_6H_6.

110. Calculation of the Percentage Composition from the Formula. — If the formula of a compound is known, and also the atomic weights of the elements composing it, the percentage composition can be calculated. Thus the formula of an iron oxide is Fe_2O_3; the atomic weight of iron is 56, of oxygen 16.

The formula represents:

$$\begin{array}{lrl} 2 \times 56, \text{ or} & 112 & \text{parts by weight of iron, and} \\ 3 \times 16, \text{ or} & \underline{48} & \text{parts by weight of oxygen, making} \\ & 160 & \text{parts by weight of iron oxide.} \end{array}$$

$\frac{112}{160}$, or 70 per cent by weight is iron, and
$\frac{48}{160}$, or 30 per cent by weight is oxygen.

111. Valence. — Among the hydrogen compounds we have so far considered is hydrogen chloride, in which the chlorine atom holds one hydrogen atom. In steam (H_2O) each oxygen atom holds two hydrogen atoms, in ammonia (NH_3) three hydrogen atoms are held by one other atom, and in methane (CH_4), four. Thus atoms

differ in their ability to hold other atoms. This holding power is expressed in terms of the power of the atom to hold hydrogen atoms. The *valence* of an atom is the number of hydrogen atoms with which it may combine or which it may replace.

Any element that combines with hydrogen, or replaces it atom for atom, has a valence of one. In the examples below, it will be seen that the metal replaces the hydrogen of the compound directly, atom for atom:

$$\begin{array}{lll} HCl, & HBr, & HI, \\ NaCl, & AgBr, & KI. \end{array}$$

If an element combines with, or replaces, two hydrogen atoms, it is said to be divalent, that is, its valence is two. A knowledge of valence is an aid in writing formulas. Valence will be considered in Chapter XVI in connection with a different property.

Sodium, potassium, silver have a valence of one. Aluminum usually has a valence of three. The other common metals usually have a valence of two.

Chlorides	Oxides
$NaCl$, KCl; $AgCl$.	Na_2O, K_2O, Ag_2O.
$ZnCl_2$; $CuCl_2$.	CaO, MgO.
$AlCl_3$.	Al_2O_3.

112. Variations in Valence. — An element may have more than one valence, according to the element with which it combines, and the conditions under which the combination takes place. The valence of hydrogen is always regarded as one, and that of oxygen as two. Sulphur has a valence of *two* in hydrogen sulphide, H_2S; in sulphur dioxide, SO_2, its valence is *four*, being twice that of oxygen; in sulphur trioxide, SO_3, its valence is *six*.

Johann Jacob Berzelius (1779–1848) was a Professor of Chemistry in Stockholm. Although hampered by lack of means, he impressed himself and his ideas on the scientific world and became the leading figure in it.

Berzelius was an analytical genius; he repeated the work and extended the laws of Dalton to organic substances. He undertook the determination of atomic weights, taking the weight of oxygen as 100. His accuracy enabled him to discover several elements. He tried to explain molecular structure and developed the electrochemical theory, which, though later modified by himself and others, has proved of great service. He introduced the use of initial letters as symbols of atoms.

CHEMICAL NAMES

The names of substances must be studied in connection with the substances and their reactions. The principles involved in the assignment of the names will aid in their recognition and explanation.

Chemical names are based largely on a system introduced by a friend of Lavoisier, Guyton de Morveau, shortly after the discovery of oxygen. *The name of a substance should show the elements of which it is composed and, as far as possible, their relative proportions.*

113. The names of elements are not based on any principle. Some, like sulphur and silver, are very old, some are named for countries or localities, as magnesium and columbium. Soda and alum were well-known compounds and when metals were obtained from them they received the names of sodium and aluminum. Other elements have been named in similar manner. Chlorine, argon, radium, and chromium are named from peculiarities possessed by them, while selenium (moon), tellurium (earth), and uranium (heaven) show that chemists have not been without poetic fancy.

Of the elements discovered more recently, the metals have received names ending in **-ium**, the non-metals in **-n** or **-ne**. The names have usually been assigned the elements by their discoverers and are carried practically unchanged into other languages.

114. Binary Compounds. — The *names of compounds* are formed by combining the names of the constituents into compound words. The name of one of the elements, a metal if present, is used adjectively and a distinctive part of the name of the other constituent is attached, as silver **chloride**, iron **oxide**, sulphur **chloride**.

Binary compounds contain only two elements and have names ending in **-ide**.

There are two compounds of mercury and oxygen. The one containing the higher oxygen ratio is mercur**ic** oxide, the one with the less oxygen is mercur**ous** oxide. In nitr**ous** oxide, the ratio of nitrogen to oxygen is 7 : 4; in nitr**ic** oxide, the ratio is 7 : 8. In general, the suffix **-ic** indicates a higher valence of the element to which it is appended than **-ous** does.

Numerical prefixes are sometimes used to indicate proportions or ratios, as carbon **mon**oxide (CO), carbon **di**oxide (CO_2).

We have defined a radical as a group of elements that seem to hold together in most chemical reactions. Many of these radicals have received special names which are used as though they were elements. The group (OH) is known as hydroxyl, (NH_4) as ammonium, (CN) cyanogen. Potassium hydroxide (KOH) and ammonium chloride (NH_4)Cl are examples of compounds containing radicals, which follow the rule for the naming of binary compounds.

115. Ternary compounds contain three elements. The name *may* end in **-ide** provided all three of the elements are indicated in the name, as sodium aluminum fluoride (Na_3AlF_6), bismuth oxychloride ($BiOCl$).

It is usual, however, for the names of compounds containing three or more elements (or radicals) to end in **-te** (*ter*, three), as potassium chlorplatinate (K_2PtCl_6). Very often a third element is not named; in this case it is to be understood that the third element is *oxygen*. Calcium sulphate ($CaSO_4$) contains calcium, sulphur, *and oxygen*.

Compounds whose names end in **-te** are very common in the class of compounds we have defined as *salts;* their

names and compositions should be associated with the corresponding *acids*.

116. Acids and Salts. — If the acid is a binary compound, it may be named as such, hydrogen chlor**ide**. The usual name of the solution is **hydro**chlor**ic** acid (HCl). The salts corresponding to these acids are named as binary compounds and have names ending in **-ide**, as sodium chloride and lead sulphide.

Many acids contain oxygen; it is not mentioned in either the systematic or popular name. The common oxygen acid of any element uses the suffix **-ic**. H_2SO_4, sulphur**ic** acid, as a ternary compound is hydrogen sulph**ate**. All salts containing (SO_4) are sulphates: K_2SO_4 potassium sulphate, $CaSO_4$ calcium sulphate.

There are compounds having the formulas H_2SO_3 and K_2SO_3: these are hydrogen sulph**ite** or sulphur**ous** acid, and potassium sulph**ite**. As already stated, the suffix **-ic** indicates a higher oxygen ratio than **-ous**. The compound with name ending in **-ate** is more highly oxidized than the one ending in **-ite**.

While our system provides names for several compounds of the same elements, it by no means follows that such compounds exist or are known. Compounds whose chemical names end in **-ite** are not at all common.

Other designations are needed occasionally, however. The highest oxygen ratio is indicated by using the prefix **per-** with the name of the salt ending in **-ate**, or of the acid ending in **-ic**. The lowest degree of oxidation is indicated by the prefix **hypo-** with the name of the salt ending in **-ite** (or the **-ous** acid).

Names and formulas should be learned in connection with the substances. The following table will, however, illustrate the principles outlined above.

NAMES OF ACIDS AND SALTS

$HClO_4$	Per-chloric acid	hydrogen perchlorate	$KClO_4$	potassium perchlorate
$HClO_3$	Chloric acid	hydrogen chlorate	$KClO_3$	potassium chlorate
$HClO_2$	Chlorous acid	hydrogen chlorite	$KClO_2$	potassium chlorite
$HClO$	Hypo-chlor-ous acid	hydrogen hypochlorite	$KClO$	potassium hypochlorite
HCl	Hydro-chloric acid	hydrogen chloride	KCl	potassium chloride

It should be borne in mind that prefixes and terminals are essential parts of chemical names, to designate particular compounds, so that *chemical names cannot be abbreviated*, and an error in spelling may designate a different compound from that intended. There is, however, a tendency among chemists to simplify the spelling of a few names, especially by the omission of final *-e*, silent.

SUMMARY

NOMENCLATURE OF ACIDS AND SALTS

I. **An acid** is a compound containing hydrogen, which can be replaced by a metal to form a salt.

II. **The name of an acid** ending in **-ic** is always obtained by adding **-ic** to the root derived from the name of the characteristic non-metallic element. In each case the formula for this acid should be committed to memory.

Chlorine forms chloric acid, $HClO_3$.

Nitrogen forms nitric acid, HNO_3.

Sulphur forms sulphuric acid, H_2SO_4.

The acid containing one less atom of oxygen than the **-ic** acid has a name ending in **-ous**; *e.g.* chlorous acid, $HClO_2$; nitrous acid, HNO_2; sulphurous acid, H_2SO_3.

Acids containing less oxygen than the **-ous** acids have the prefix **hypo-** and end in **-ous**; *e.g.* hypochlorous acid, $HClO$.

Acids containing no oxygen have the prefix **hydro-** and end in **ic**; *e.g.* hydrochloric acid, HCl.

These rules for the names of acids apply only to those acids commonly classed among the inorganic compounds.

III. Acids having the prefix **hydro-** and ending in **-ic** form **salts** with names ending in **-ide** and having no prefix.

All other acids with names ending in **-ic** form salts with names ending in **-ate**.

All acids whose names end in **-ous** form salts whose names end in **-ite**.

Some Acids and their Salts

Name of Acid	Formula	Salts Formed	Illustrations of Salts
1. Hydrochloric acid	HCl	Chlorides	$NaCl$, sodium chloride
2. Sulphuric acid . .	H_2SO_4	Sulphates	$CuSO_4$, copper sulphate
3. Nitric acid	HNO_3	Nitrates	$Pb(NO_3)_2$, lead nitrate
4. Sulphurous acid . .	H_2SO_3	Sulphites	K_2SO_3, potassium sulphite
5. Hydrobromic acid .	HBr	Bromides	$AgBr$, silver bromide
6. Carbonic acid . .	H_2CO_3	Carbonates	$CaCO_3$, calcium carbonate
7. Hydrosulphuric acid	H_2S	Sulphides	ZnS, zinc sulphide
8. Hydriodic acid . .	HI	Iodides	KI, potassium iodide
9. Nitrous acid . . .	HNO_2	Nitrites	$NaNO_2$, sodium nitrite
10. Phosphoric acid . .	H_3PO_4	Phosphates	$FePO_4$, iron phosphate
11. Hydrofluoric acid .	HF	Fluorides	CaF_2, calcium fluoride
12. Chloric acid . . .	$HClO_3$	Chlorates	$KClO_3$, potassium chlorate

EXERCISES

1. Define and illustrate (*a*) a symbol; (*b*) a chemical formula.

2. State the meaning of every symbol and figure in each of the following formulas: HCl; H_2SO_4; $5\,CO_2$; $Ca(NO_3)_2$; $CuSO_4 . 5\,H_2O$.

3. How many atoms of hydrogen in each of the following: HBr; H_2SO_4; NH_3; $NH_4C_2H_3O_2$; $(NH_4)_2Fe_2(SO_4)_4 . 24\,H_2O$?

4. Making use of the table of atomic weights in the Appendix, calculate the molecular weights of the following compounds: CuO; H_2SO_4; $KClO_3$; $ZnCl_2$; $NaOH$.

5. Determine the vapor density of each of the following gases: O_2; O_3; HCl; CO_2; NH_3.

6. Calculate the weight of a liter of each of the following gases (standard conditions): H_2; CO_2; NH_3; SO_2; CO.

7. Acetylene gas has the formula C_2H_2. What is the weight of a liter of it (standard conditions)?

8. What per cent of potassium chlorate, $KClO_3$, is oxygen?

9. If a sample of washing soda has a composition represented by the formula $Na_2CO_3 . 10\,H_2O$, what per cent of it is water of crystallization?

10. A hundred grams of a compound contain 30.43 grams of nitrogen and 69.57 grams of oxygen. What per cent of the compound is nitrogen and what per cent is oxygen? What is the ratio between the number of nitrogen atoms and the number of oxygen atoms? What is the simplest formula that could be used to express the composition of the compound?

11. A substance on analysis was found to contain carbon 40 %, hydrogen 6.67 %, and oxygen 53.33 %. What is the simplest formula that could be used to represent such a substance?

12. Calculate the percentage composition of crystallized barium chloride ($BaCl_2$, $2\,H_2O$).

13. Calculate the percentage of water of crystallization in crystalline copper sulphate, $CuSO_4 . 5\,H_2O$.

Calculate formulas from the following data:

Name	Vapor Density	Percentage Composition	
		Carbon	Hydrogen
14. Methane	8	75	25
15. Ethane	15	80	20
16. Propane	22	81.81	18.18
17. Butane	29	82.75	17.24

18. What weight of mercury could be obtained from 500 pounds of cinnabar, HgS?

19. What weight of copper would be obtained from 250 grams of copper sulphate, $CuSO_4$?

20. Calculate the empirical (simplest) formula of a compound containing calcium 29.41 %, oxygen 47.06 %, and sulphur 23.53 %.

21. The vapor density of a certain gas is 14. What is the molecular weight of the gas? It is composed of carbon 42.8 % and oxygen 57.1 %. What is its formula?

22. Alcohol, a liquid at ordinary temperatures, is readily converted into a gas; 0.247 gram of the gas has a volume of 184.9 c.c. at a temperature of 150° C. What is the vapor density of the gas? What is the molecular weight of alcohol? Alcohol is composed of carbon 52.2 %, hydrogen 13.0 %, oxygen 34.8 %. Determine its formula.

23. 0.55 gram of a certain gas has a volume of 277.7 c.c. at standard conditions. The gas is composed of nitrogen 63.6 %, oxygen 36.3 %. What is the formula of the substance?

24. 0.35 gram of a liquid that is easily vaporized has, in the gaseous form, a volume of 99.7 c.c. (corrected). The substance is composed of carbon 92.3 %, hydrogen 7.7 %. Determine the formula of the substance.

25. Describe an experimental method of proving that aluminum is trivalent, assuming that the atomic weight is known.

CHAPTER XIII

CHEMICAL EQUATIONS

117. Representation of Chemical Reactions by Equations. — Since the symbol of an element and the formula of a compound represent more than the name, we may use them instead of the names in the equations we have employed, and then the equation will represent definite masses as taking part in the reaction.

These equations are not algebraic; they represent changes that actually take place. They cannot, therefore, be predicted with certainty. When we know by experiment:

(1) that substances will react;
(2) the composition of each substance;
(3) all the products formed;
(4) the composition of each product,

we can represent the reaction by an equation, and calculate the relative quantities involved.

The fundamental principle upon which chemical calculations depend is the indestructibility of matter, so the equation must represent the same amount of each element after the change as before. There must be the same number of atoms of each element represented on each side of the equation.

118. How an Equation is Written. — The reacting substances are usually written first, on the left; the products

on the right; the arrow (or the equality sign) is not to be read "equal to," but *yield* or *form;* the addition sign *with.* As the change may occur under different conditions, no attempt is made to represent *how* the action occurred.

In order to show how an equation is balanced, the equation for the decomposition of potassium chlorate will be taken up in detail. On heating potassium chlorate, two products result, potassium chloride and oxygen. Potassium chlorate has the composition shown by the formula $KClO_3$; potassium chloride, KCl; and we have shown (§ 97) that there are two atoms in the molecule of oxygen, O_2. Using these formulas, we have: $KClO_3 \longrightarrow KCl + O_2$; but it will be seen that there are three atoms of oxygen on the left and only two on the right-hand side of the equation. An equal number of atoms, however, must appear on each side. In order that the quantities and compositions shall be correctly represented, it is necessary that suitable coefficients be supplied, so that the equation will balance. The equation will then read:

$$2\ KClO_3 \longrightarrow 2\ KCl + 3\ O_2$$

In this equation, we have on each side 2 atoms of potassium, 2 of chlorine, and 6 of oxygen.

Materials which are present, but which undergo no change, such as water in which the substances are dissolved, catalytic agents, etc., are not expressed in the equation.

119. Equations for Reactions already Studied. — In the sections which follow, the equations for the chemical changes already studied are correctly given. In order to master these, the following method is recommended:

During the study of this chapter, the student should constantly review the reactions which the equations repre-

sent. He should turn back to the word equations already given where the reactions were originally described, if the heading of the paragraph does not recall the equations to his mind. The word equation for each reaction should next be written, the formula for each compound placed beneath its name, and the equation balanced without reference to the text. The final equation should then be verified. Each important equation in the succeeding chapters should be studied in the same way.

120. Oxides and Oxygen. — The heating of carbon, sulphur, and iron in the air results in the formation of an oxide of the element heated in each case (§ 25). The equations are:

$$C + O_2 \longrightarrow CO_2$$
$$S + O_2 \longrightarrow SO_2$$
$$3\,Fe + 2\,O_2 \longrightarrow Fe_3O_4$$

The slow oxidation of phosphorus, made use of in the analysis of air, and the burning of phosphorus in oxygen (Fig. 10) are both represented by the equation:

$$4\,P + 5\,O_2 \longrightarrow 2\,P_2O_5$$

Thus we find that the product, phosphorus pentoxide, is the same whether the phosphorus combines with the oxygen slowly and quietly, or rapidly and violently. All the above equations illustrate the process of *direct combination*, or *synthesis*.

The production of oxygen from mercuric oxide and from potassium chlorate illustrates the opposite process, *simple decomposition*, or *analysis*. The equations are:

$$2\,HgO \longrightarrow 2\,Hg + O_2$$
$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

121. Hydrogen. — The equation for the *preparation of hydrogen* by electrolysis of water (§ 33) is:

$$2\,H_2O \longrightarrow 2\,H_2 + O_2$$

When sodium reacts on water, we have:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

For the formation of hydrogen by the reaction between metals and acids, we have the following equations:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Mg + 2\,HCl \longrightarrow MgCl_2 + H_2$$

The formulas of sulphuric acid and zinc sulphate show very clearly how the latter is produced by the replacement of the hydrogen of the acid by the zinc. The formation of sodium hydroxide and magnesium chloride in the equations given above furnish other examples of *simple replacement*.

122. The Formation of Water by the burning of hydrogen in oxygen or in air (§ 37) is represented by the equation:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

It will be noticed that this is the exact reverse of the equation given above for the decomposition of water. A large proportion of our equations are *reversible;* that is, the direction in which the reaction proceeds depends upon the conditions. This may be shown by the use of the double arrow, so we may write the equation:

$$2\,H_2 + O_2 \rightleftarrows 2\,H_2O$$

The reduction of copper oxide by hydrogen (§ 38) is expressed by the equation:

$$CuO + H_2 \longrightarrow Cu + H_2O$$

Hydrogen has a great tendency to unite with oxygen, and so takes this element away from the copper.

123. Preparation of Chlorine by electrolysis of brine (§ 74) is represented by the equation:

$$2\,NaCl + 2\,H_2O \longrightarrow 2\,NaOH + H_2 + Cl_2$$

This equation represents the final result of the reaction, and does not show the intermediate steps; viz. the separation of the sodium and chlorine, and the reaction of the former with the water to form sodium hydroxide.

The liberation of chlorine by the oxidation of hydrochloric acid in the presence of a catalytic agent (§ 75) is represented by the equation:

$$4\,HCl + O_2 \longrightarrow 2\,H_2O + 2\,Cl_2$$

When manganese dioxide is used as the oxidizing agent, the equations are:

$$MnO_2 + 4\,HCl \longrightarrow MnCl_2 + 2\,H_2O + Cl_2$$

$$MnO_2 + 2\,NaCl + 2\,H_2SO_4 \longrightarrow MnSO_4 + Na_2SO_4 + 2\,H_2O + Cl_2$$

A comparison of these three equations shows the formation of water and chlorine in each case. We shall see from the equation for the formation of hydrochloric acid given below that in all three methods we may regard the liberation of the chlorine as the result of the oxidation of the hydrogen of hydrochloric acid. One atom of oxygen in the manganese dioxide oxidizes two molecules of hydrochloric acid.

124. Chlorides. — The following equations represent the reaction of chlorine with various substances, resulting in the *formation of chlorides* (§§ 77–79):

$$\begin{aligned}
H_2 \; + Cl_2 &\longrightarrow 2\,HCl \\
2\,Sb + 3\,Cl_2 &\longrightarrow 2\,SbCl_3 \\
Zn \; + Cl_2 &\longrightarrow ZnCl_2 \\
H_2O + Cl_2 &\longrightarrow 2\,HCl + O
\end{aligned}$$

The last equation represents the liberation of ***nascent oxygen***, in the bleaching by chlorine, so we write the symbol O, indicating the oxygen *atom*, and not O_2, indicating the oxygen molecule. It will be seen that this equation is the reverse of that given above for the preparation of chlorine, except that in that case the oxygen is not represented as nascent, but as ordinary oxygen, and the equation is balanced accordingly.

125. Hydrochloric Acid. — Two methods for producing *hydrochloric acid* are indicated in the equations just given. We may represent its formation from salt and sulphuric acid (§ 82) as follows:

$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl$$

This equation illustrates *double replacement* or ***metathesis***, more often called double decomposition; each compound apparently breaks up into two parts, each of which unites with a different part of the other compound. Such reactions can only be prevented from becoming reversible by the removal of one of the products from the field of action; in this case hydrogen chloride is driven off as a gas. Double replacements are common in solutions.

126. Test for a Chloride. — As a typical reaction illustrating this test, we may take the reaction of sodium chloride with silver nitrate (§ 88):

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

The products of the double replacement in this case are silver chloride and sodium nitrate. This reaction is prevented from becoming reversible by the fact that silver chloride, being insoluble, is precipitated, and so is removed from the field of action as rapidly as it is formed.

SUMMARY

Chemical reactions are represented by equations in which the reacting substances are written on the left and the products on the right, separated by an equality sign or an arrow.

Equations represent actual chemical changes and must represent the same amount of each element after the change as before. The composition of each reacting substance and of all the products must be known before the equations can be written. Catalytic agents, and solvents that are unaffected are not expressed in the equation. The conditions of the chemical action are not indicated by the equation.

Equations may represent processes of:

(*a*) direct combination;
(*b*) decomposition;
(*c*) simple replacement;
(*d*) double replacement;
(*e*) oxidation and reduction.

A reversible reaction is one in which the reaction may proceed in either direction according to conditions. A reaction will not be reversible if one of the products is eliminated as a gas or as an insoluble substance during the reaction.

EXERCISES

1. Write an equation for (*a*) a synthesis, (*b*) an analysis.

2. Distinguish between analysis and synthesis.

3. Write the equation for the reaction that takes place when potassium, a metal similar to sodium, reacts with water. What process does the equation represent?

4. Write a reversible equation involving hydrogen and chlorine. Tell how you can control the direction in which the action proceeds.

5. Write the equation for the reaction that might reasonably be expected to occur if sodium chlorate, $NaClO_3$, is heated.

6. Write the equation for the reaction of potassium chloride, KCl, with sulphuric acid. Name the process and the products. Explain why the reaction is not ordinarily reversible.

7. Distinguish between simple replacement and double replacement.

8. Write the equation for a laboratory preparation of chlorine.

9. Write the equation expressing the reaction of magnesium with oxygen; with sulphuric acid; with chlorine; and with hydrochloric acid.

Name the products and the process illustrated in each case.

10. Explain what is meant by double replacement and illustrate it by an equation.

11. Complete and balance the following equations, using formulas throughout:

manganese dioxide + hydrochloric acid ⟶
hydrogen + hot copper oxide ⟶
phosphorus + oxygen ⟶
calcium + hydrochloric acid ⟶

12. Express the following in symbols and formulas and complete the chemical equations:

(*a*) the action of dilute sulphuric acid on zinc;
(*b*) the reaction between silver nitrate and barium chloride.

13. Write an equation representing zinc as taking part in a synthesis. In a simple replacement.

14. What types of chemical change are represented by each of the following:

$$2\,K + 2\,H_2O \longrightarrow 2\,KOH + H_2$$
$$Mg + Cl_2 \longrightarrow MgCl_2$$
$$2\,NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,H_2O$$
$$Mg(OH)_2 \longrightarrow MgO + H_2O$$
$$Fe_3O_4 + 4\,H_2 \rightleftarrows 3\,Fe + 4\,H_2O$$

15. Write the equation for the reaction between silver nitrate and barium chloride, $BaCl_2$.

16. Tin dioxide, SnO_2, is formed by heating tin in air. Write the equation.

17. Write the equation for the reaction in the oxy-hydrogen blowpipe.

18. Write the equations for:

(*a*) potassium taking part in a simple replacement.
(*b*) the potassium in the compound formed participating in a double replacement.

19. Write the reversible equation for the actions by which Lavoisier proved what happened when a metal was heated in air.

20. Write the equation showing the formation of zinc chloride, $ZnCl_2$, from zinc.

CHAPTER XIV

CHEMICAL CALCULATIONS

The calculations from chemical equations may be divided into three classes: those involving weight only, those involving volume only, and those involving both weight and volume. Each type of problem will be separately discussed.

127. Calculation of Relative Weights from the Equation. — In the equation

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2,$$

the molecule of potassium chlorate weighs

$$39 + 35.5 + 3 \times 16\ (122.5);$$

the molecule of potassium chloride weighs

$$39 + 35.5\ (74.5);$$

the oxygen molecule weighs

$$2 \times 16\ (32).$$

That is, 2×122.5, or 245 parts by weight of potassium chlorate, on being decomposed, give 2×74.5 (149) parts of potassium chloride, and 3×32 (96) parts of oxygen.

$$\begin{array}{cccc} 2\,KClO_3 \longrightarrow & 2\,KCl & + & 3\,O_2 \\ 2 \times 122.5 & 2 \times 74.5 & & 3 \times 32 \\ 245 & 149 & & 96 \end{array}$$

Now *the same relation exists between the actual weights expressed in grams, pounds, tons, etc., as exists between the chemical weights represented by the equation.*

Suppose we wish to prepare 20 grams of oxygen; how much potassium chlorate must be used? The numbers we have calculated from the equation show that 245 grams of potassium chlorate produce 96 grams of oxygen, or, in other words, that the weight of potassium chlorate is about $2\frac{1}{2}$ times that of the oxygen evolved. It appears, therefore, that we shall need *about* 50 grams of potassium chlorate to obtain 20 grams of oxygen. The exact number can be obtained from the proportion:

$$96 : 245 :: 20 \text{ grams} : x \text{ grams}$$
$$96\,x = 4900$$
$$x = 51.0 \text{ grams, the potassium chlorate needed}$$

This answer agrees with the result of our previous mental calculation. It is well to thus make a preliminary mental approximation in every case before stating the arithmetical proportion.

What quantity of sulphuric acid (H_2SO_4) is needed to exactly decompose 100 grams of sodium chloride, when sodium sulphate and hydrogen chloride are formed?

The solution of the problem may be briefly stated as follows:

$$\begin{array}{lcl} \text{100 grams} & & x \text{ grams} \\ \quad 2\,NaCl & + & H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl \\ \quad 117 & & \quad 98 \end{array}$$

$$\begin{array}{ll} Na = 23 & H_2 = 2 \\ Cl = \underline{35.5} & S = 32 \\ \quad 58.5 \times 2 = 117 & O_4 = \underline{64} \\ & \qquad 98 \end{array}$$

$$117 : 98 :: 100 \text{ grams} : x \text{ grams}$$
$$x = 83.8 \text{ grams, sulphuric acid required}$$

It will be noticed that only the reacting weights of the *two substances involved* in this particular problem, one

whose weight is given and one whose weight we wish to find, have been used.

Similarly, and as though it were a new problem, the weight of the sodium sulphate might be found:

$$\underset{117}{\overset{100 \text{ grams}}{2\,NaCl}} + H_2SO_4 \longrightarrow \underset{142}{\overset{x \text{ grams}}{Na_2SO_4}} + 2\,HCl$$

$$\begin{array}{ll} Na = 23 & \\ Cl = \underline{35.5} & \\ \quad 58.5 \times 2 = 117 & \end{array} \qquad \begin{array}{lr} Na_2 = & 46 \\ S \;\;= & 32 \\ O_4 \;= & \underline{64} \\ & 142 \end{array}$$

$$117 : 142 :: 100 \text{ grams} : x \text{ grams}$$

$$x = 121.3 \text{ grams, sodium sulphate produced}$$

By the same method we may find the weight of the hydrogen chloride:

$$\underset{117}{\overset{100 \text{ grams}}{2\,NaCl}} + H_2SO_4 \longrightarrow Na_2SO_4 + \underset{73}{\overset{x \text{ grams}}{2\,HCl}}$$

$$\begin{array}{ll} Na = 23 & \\ Cl = \underline{35.5} & \\ \quad 58.5 \times 2 = 117 & \end{array} \qquad \begin{array}{l} H = 1 \\ Cl = \underline{35.5} \\ \quad 36.5 \times 2 = 73 \end{array}$$

$$117 : 73 :: 100 \text{ grams} : x \text{ grams}$$

$$x = 62.4 \text{ grams, hydrogen chloride produced}$$

128. Calculation of Relative Volumes from the Equation. — The method in the preceding paragraphs applies to *the weights* of all substances, solid, liquid, or gaseous. But in the case of gases, we found the formula has a meaning that did not apply to liquids or solids (cf. § 106).

Problems involving *volume only* are simple to solve, because the *relation between the numbers of molecules of the*

gases represented in the chemical equation is the same as that between the volumes of these gases (§ 96).

In the equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

it appears that two molecules of hydrogen react with one molecule of oxygen to form two molecules of steam. Since equal numbers of molecules occupy equal volumes, the volume of the hydrogen must be twice that of the oxygen and equal to that of steam.

In the equation:

$$2\,H_2O + 2\,Cl_2 \longrightarrow 4\,HCl + O_2$$

we see that *two molecules* of chlorine are used to liberate one molecule of oxygen, hence two volumes of chlorine will furnish one volume of oxygen. Therefore, *in the case of gases*, the coefficients represent the *relative volumes of the substances.*

The equation

$$H_2 + Cl_2 \longrightarrow 2\,HCl$$

may be read: 1 part by volume of hydrogen with 1 part by volume of chlorine will give 2 parts by volume of hydrogen chloride; and also 2 parts by weight of hydrogen and 71 parts by weight of chlorine give 73 parts by weight of hydrogen chloride.

Suppose that we are required to calculate how many liters of oxygen would be liberated by the complete reaction of 12 liters of chlorine with water. The problem and its solution may be stated as follows:

$$\begin{array}{ccccccccc} & & \text{12 liters} & & & & x\text{ liters} \\ 2\,H_2O & + & 2\,Cl_2 & \longrightarrow & 4\,HCl & + & O_2 \\ & & \text{2 vol.} & & & & \text{1 vol.} \end{array}$$

$$2 : 1 :: 12 \text{ liters} : x \text{ liters.}$$

$$x = 6 \text{ liters, volume of oxygen liberated.}$$

129. Problems involving Both Weight and Volume include cases in which the object is to determine the weight of a certain compound required for the production of a given volume of a gas, or *vice versa.* Two methods for the solution of this type of problem are given in this and the following sections. The method to be employed by a particular class of students will be determined by the method already selected for the determination of molecular weights (§§ 101, 102).

The first method is shown by the solution of the following problems:

How many liters of a gas can be obtained by heating 20 grams of mercuric oxide? First, write the equation and calculate the number of *grams* of oxygen by the method given in § 127.

$$\begin{array}{lcccc} \text{20 grams} & & & & x \text{ grams} \\ 2\,HgO & \longrightarrow & 2\,Hg & + & O_2 \\ 432 & & & & 32 \end{array}$$

$$\begin{array}{ll} Hg = 200 & \qquad O_2 = 32 \\ O \;\,= \underline{\;16} & \\ 216 \times 2 = 432 & \end{array}$$

$$432 : 32 :: 20 \text{ grams} : x \text{ grams}$$

$$x = 1.48 \text{ grams oxygen.}$$

But the problem asks for the number of liters of oxygen.

We can always find the approximate weight of 1 liter of a gas from the molecular weight (§ 101):

$\frac{32}{2} = 16$, V.D. of oxygen. $\therefore$ 1 liter of oxygen weighs $16 \times 0.09 = 1.44$ grams. Hence

$$\frac{1.48}{1.44} = 1.027 \text{ liters, oxygen produced.}$$

How many grams of potassium chlorate must be heated to obtain 10 liters of oxygen?

In this type of problem, as we have not the real weight given, we must calculate it from the number of liters given. The first step in the problem is to find the weight of the given volume of oxygen. The second step is a problem of the usual type, with one weight given, to find the other. The two steps are given in detail below.

(I) $\frac{32}{2} = 16$, V.D. of oxygen.

$\therefore$ 1 liter of oxygen weighs $16 \times 0.09 = 1.44$ grams.

$10 \times 1.44 = 14.4$ grams, weight of oxygen.

(II)

$$\begin{array}{lcll} x \text{ grams} & & & 14.4 \text{ grams} \\ 2\,KClO_3 & \longrightarrow & 2\,KCl \;+ & 3\,O_2 \\ \;\;245 & & & 96 \end{array}$$

$$\begin{array}{ll} K = 39 & \qquad\qquad O_2 = \underline{32} \\ Cl = 35.5 & \qquad\qquad 32 \times 3 = 96 \\ O_3 = \underline{48} & \\ 122.5 \times 2 = 245 & \end{array}$$

$245 : 96 :: x \text{ grams} : 14.4 \text{ grams}$

$x = 36.8$ grams, potassium chlorate required.

130. Problems involving Both Weight and Volume: Direct Method. — The volume of gases reacting can be directly calculated from the equation, if we keep in mind the following fact (§ 102): when weights are expressed in grams, every gram-molecule of gas represented by the equation stands for 22.~~2~~4 liters. From the relations between the units it is also true that, when weights are expressed in kilograms, every kilogram-molecule of the gas stands for 22.~~2~~4 cubic meters; and when weights are expressed in ounces (Avoirdupois), each ounce-molecule of gas stands for 22.~~2~~4 cubic feet.

Suppose we wish to produce 50 liters of hydrogen by the reaction:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

65 grams of zinc give 2 grams of hydrogen. But 2 grams of hydrogen is a *gram-molecule* of hydrogen, and occupies 22.2 liters. Hence 65 grams of zinc give 22.2 liters of hydrogen. The problem may then be stated as follows:

$$\begin{array}{lcccc} x \text{ grams} & & & & 50 \text{ liters} \\ \quad Zn & + H_2SO_4 & \longrightarrow & ZnSO_4 + & H_2 \\ 65 \text{ grams} & & & & 22.2 \text{ liters} \end{array}$$

$Zn = 65$ | $H_2 = 1$ molecule of hydrogen and in this problem stands for 22.2 liters

$$22.2 \text{ liters} : 50 \text{ liters} :: 65 \text{ grams} : x \text{ grams}$$

$$x = 146.4 \text{ grams, zinc needed.}$$

In the decomposition of potassium chlorate:

$$2\,KClO_3 \longrightarrow 2\,KCl + 3\,O_2$$

only one of the substances is gaseous; 245 grams of potassium chlorate give 3 gram molecules of oxygen ($3\,O_2$), which occupy 3×22.2 liters. If we wish to produce 100 liters of oxygen, we can find the weight of potassium chlorate needed, by the following solution:

$$\begin{array}{lcccc} x \text{ grams} & & & & 100 \text{ liters} \\ 2\,KClO_3 & \longrightarrow & 2\,KCl & + & 3\,O_2 \\ \quad 245 & & & & 3 \times 22.2 \text{ liters} \end{array}$$

$$\begin{array}{ll} K & = 39 \\ Cl & = 35.5 \\ O_3 & = \underline{48} \\ & 122.5 \times 2 = 245 \end{array} \qquad 3 \times 22.2 = 66.6$$

$$66.6 \text{ liters} : 100 \text{ liters} :: 245 \text{ grams} : x$$

$$x = 367.9 \text{ grams, potassium chlorate needed.}$$

SUMMARY

The **relative weights** of the different substances in a chemical equation can be calculated. Such calculations deal with *but two* of the substances at a time. The weights of the substances are in the same ratio as the weights of the molecules involved. With the weight in grams of one of the substances known, and the weights of the molecules ascertained, a proportion is formed with these three quantities. The weight in grams of the second substance is found by solving the proportion.

Relative volumes of gaseous substances are represented by the coefficients of their molecules in an equation.

Problems involving weight and volume may be solved by finding the weight of the gas involved and then forming a proportion including the 3 known quantities and the unknown quantity. It is sometimes convenient to make use of the fact that, when weights are expressed in grams, each molecule of the gas represented in the chemical equation stands for 22.4 liters.

EXERCISES

1. Calculate the weight of oxygen obtained from heating 36 grams of mercury oxide.

2. How many grams of copper were heated to form 2.64 grams of copper oxide?

3. 2.4 grams of zinc were treated with an excess of dilute sulphuric acid. Calculate weight of each product formed.

4. Find how many grams (*a*) of potassium chloride, KCl, and (*b*) of sulphuric acid are needed to produce 2.8 grams of hydrogen chloride.

5. Calculate the weight of manganese dioxide and that of hydrogen chloride used to produce 4.8 grams of chlorine. How many grams of manganese chloride were formed?

6. How much sodium chloride, reacting with sulphuric acid, would be necessary to produce 10 grams of dry sodium sulphate? $2 NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2 HCl$

7. An experiment showed that, when 2.16 grams of silver were treated with chlorine, 2.87 grams of silver chloride were formed. Calculate from this result the atomic weight of silver.

8. How much zinc is required to prepare 10 grams of crystallized zinc sulphate, $ZnSO_4 \cdot 7\,H_2O$?

9. What weight of oxygen is required to unite with 21 grams of iron to give the magnetic oxide of iron, Fe_3O_4? What volume will this oxygen occupy at 10° C. and 750 mm.?

10. State the relative volumes of each gaseous substance indicated by the equations representing:

(*a*) hydrogen combining with chlorine;
(*b*) chlorine combining with water;
(*c*) hydrogen combining with bromine;
(*d*) electrolysis of sodium chloride.

11. 30 c.c. of hydrogen are mixed with 40 c.c. of air that contains 20 % of oxygen, and the mixture is ignited. What gases remain after explosion and what is the volume of each? All gas volumes in this question are to be considered at standard conditions.

12. How many volumes of oxygen are required to burn one volume of methane (CH_4) to carbon dioxide and water?

13. How many liters of oxygen at standard conditions can be obtained by heating 8.4 grams of potassium chlorate?

14. How many liters of oxygen at standard conditions would be formed by the complete decomposition of 25 grams of mercuric oxide?

15. What volume of oxygen, under standard conditions, could be obtained by the electrolytic decomposition of 2 grams of water?

$2 H_2O \rightarrow 2 H_2 + O_2$

16. What volume of hydrogen measured under standard conditions is required to reduce 11.94 grams of copper oxide? What is the weight and what is the volume of the liquid (water) formed?

17. How many grams of zinc sulphate would be formed during the production of 250 liters of hydrogen by the reaction between zinc and diluted sulphuric acid?

18. How many grams of potassium chlorate would be required for the preparation of 10 liters of oxygen at standard conditions?

19. How many grams of mercuric oxide are required for the preparation of 8 liters of oxygen under standard conditions?

20. How many grams of zinc are necessary for the production of 90 liters of hydrogen measured under standard conditions, by the action of hydrochloric acid on the metal?

21. How many grams of sodium chloride would be required for the preparation by electrolysis of 29.4 liters of chlorine at 750 mm. and 21° C?

22. How many kilograms of iron would be required to furnish hydrogen enough to fill a balloon of 6350 cubic meters capacity?

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

CHAPTER XV

I Na SODIUM AND POTASSIUM K. I

131. Preparation of Sodium. — The great chemical activity of sodium and the stability of its compounds made the preparation of metallic sodium a difficult chemical problem. Like many others, it was solved by the application of electricity. Sir Humphry Davy, in 1807, obtained both sodium and potassium by the electrolysis of the melted hydroxides, and the metals are now prepared commercially by this method (Fig. 36).

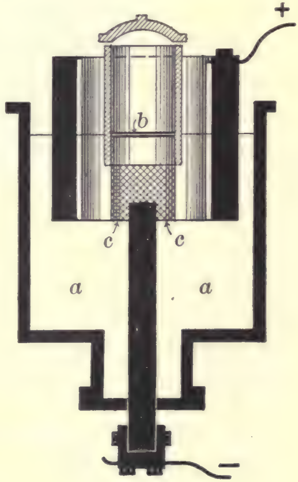


FIG. 36.

The sodium hydroxide is contained in an iron pot, in which it is melted. The cathode is an iron rod coming up through the bottom of the cylinder. The anode is an iron or nickel cylinder coming down from the top and surrounding the cathode. A metal cylinder with removable cover is suspended so as to come down inside the anode cylinder.

When the current is passed through the melted hydroxide, the sodium and hydrogen appear at the cathode and the oxygen at the anode. Suspended from the metal cylinder is a cylinder of wire gauze (*c*, *c*) through which

the fused hydroxide (*a*) can pass, but which prevents the passage of bubbles of the gas or globules of melted sodium. The molten sodium, being lighter than the melted hydroxide, rises to the surface (*b*) above the cathode, and is ladled off from time to time. The hydrogen escapes through holes in the cover and the oxygen is led off through a pipe from the side. The reasons for these precautions will be readily understood when we keep in mind the energy with which oxygen combines with both sodium and hydrogen. The heat generated by the passage of the current is sufficient to keep the hydroxide molten after the action starts. The equation for the electrolysis is:

$$2\,NaOH \longrightarrow 2\,Na + O_2 + H_2$$

132. Physical Properties of Sodium. — Sodium is a silver-white metal, possessing a brilliant luster when in a pure state. It is soft enough at ordinary temperatures to be readily cut with a knife and to be molded by the fingers. It may be formed into wire by pressing it through a hole in a metal plate. It is a very light metal, slightly less dense than water. It is a good conductor of heat and of electricity. Other properties of sodium, however, prevent its practical use as an electric conductor. "Metallic" luster and conductivity of heat and electricity are characteristic physical properties of metals.

133. Chemical Activity. — Sodium is in general a very active element chemically. It burns readily in oxygen and in chlorine, and is an energetic reducing agent. The color of its flame is bright yellow, and this color is imparted to a non-luminous flame when any sodium compound is heated in it.

134. Action with Water. — The most striking chemical property of sodium is its action with water. Exposed to

Sir Humphry Davy (1778–1829) was the most brilliant of English investigators. He early appreciated the value of the atomic theory and adopted it. He discovered the anesthetic properties of nitrous oxide. He made a very extended study of the effect of passing an electric current through substances and solutions, discovering by this means several new elements, notably sodium and potassium.

Davy explained the chemical nature of acids as compounds of hydrogen, a view not hitherto held. He announced chlorine as an element. He is famed as the inventor of the miner's safety lamp.

For seven years he was president of the Royal Society of England.

moist air, it tarnishes almost instantly on account of the formation of a layer of sodium hydroxide. In perfectly dry air, it remains unchanged at ordinary temperatures. When thrown on water, it skims over the surface with a hissing sound (§ 34). The water is rapidly decomposed, one half the hydrogen being set free, and the sodium combines with the oxygen and the other half of the hydrogen to form sodium hydroxide:

$$2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$$

The hydroxide dissolves in water and may be obtained by evaporation. A large amount of energy is liberated in the decomposition of water by sodium, which may be readily shown by dropping a piece of sodium on a moist piece of filter paper. In this way the heat is all liberated at one place and is sufficient to ignite the hydrogen. On account of its ready action with water, the sodium is always kept under kerosene or some other oil containing no oxygen, or in air-tight containers.

135. Uses of Sodium. — This metal is used for making sodium peroxide, sodium cyanide, and many complex compounds used as dyes and drugs. Its chemical activity makes it valuable for the laboratory study of typical chemical reactions.

136. Spectrum Analysis. —The colors imparted to flames by different elements furnish a simple and valuable method of analysis. The different colors found in light are bent to different degrees in passing through a prism, and are so separated from each other. The band of light thus produced is known as a *spectrum*, and the instrument used to produce and view the spectrum is called a *spectroscope*. It was invented by Bunsen and Kirchhoff. The light to be

studied is admitted through a narrow slit (A) in the end of a tube, in such a way that it will fall in parallel rays on a prism (C) with its edges parallel to the slit. When the beam emerges from the prism, the different colors are separated and the spectrum is viewed through lenses (E) placed at the end of another tube (Fig. 37).

White light, produced by an incandescent solid, gives a spectrum consisting of a continuous band of color, shading from red through orange, yellow, green, blue, and indigo to violet. When the light is due to incandescent vapors, the spectrum consists of a series of bright lines, the color and position of which differ for each element.

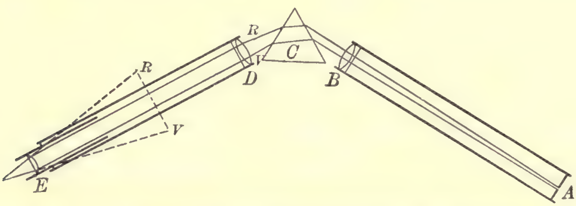


FIG. 37. — DIAGRAMMATIC REPRESENTATION OF SPECTROSCOPE.

The yellow color spoken of above is due to the presence of sodium vapor in the flame. This may be most conveniently produced by placing in a flame a rod of common glass, which contains a sodium compound. Such a flame when viewed with a good spectroscope shows two yellow lines very close together. The spectrum of potassium consists of a double line in the violet end and a line in the red end of the spectrum.

Lithium is a rare metal closely related to sodium and potassium. It was thought to exist in very few minerals until the spectroscope showed that small quantities of it were widely distributed throughout nature. Its spectrum consists of a bright red line and a very faint yellow line.

The presence of one millionth of a milligram of lithium can be shown by means of the spectroscope.

The observance of unfamiliar lines in the spectra of known elements has led in several instances to the discovery of elements. By its spectrum, helium was known to exist in the sun before this element was found in the earth. The frontispiece shows the spectrum of the sun, and that of a number of elements. The last two elements are metals of the rare earths, præsodymium and neodymium respectively.

137. Bases. — A solution of sodium hydroxide turns red litmus blue, an action exactly the reverse of that of an acid. Substances behaving like sodium hydroxide in this respect are said to have an *alkaline reaction.*

If we mix solutions containing weights of hydrochloric acid and sodium hydroxide proportional to their molecular weights, there is a rise of temperature, and the resulting solution affects neither red nor blue litmus. This solution contains sodium chloride, a fact that is clearly indicated by its taste. As the acid and the hydroxide have both lost their characteristic properties, the resulting solution is said to be *neutral* and the process is known as *neutralization.* The change may be expressed by the equation:

$$HCl + NaOH \longrightarrow H_2O + NaCl$$

Sodium hydroxide, because of its action with acids, is a typical base. A *base* is the hydroxide of a metal or of a metallic radical. It may or may not be soluble in water. Copper hydroxide is an illustration of a base which is insoluble in water. Water solutions of bases give alkaline reactions. Potassium hydroxide and calcium hydroxide are two other common soluble bases.

138. Preparation of Potassium. — Potassium resembles sodium in so many respects that it may be very briefly discussed.

Its preparation is similar to that of sodium, substituting potassium hydroxide for sodium hydroxide.

139. Properties of Potassium. — Potassium is a silvery white metal with a slight bluish tinge. It is softer than sodium, lighter, and melts at a lower temperature. Although sodium and potassium are solids at ordinary temperatures, an alloy of the two can be prepared that is a liquid.

The chemical properties of potassium closely resemble those of sodium, but it is more active. It decomposes water, forming potassium hydroxide and liberating hydrogen. The energy produced is sufficient to ignite the hydrogen, as the potassium skims over the surface (Fig. 16, page 35). Potassium imparts a reddish violet color to the flame. As the presence of a slight trace of sodium obscures the potassium flame, several thicknesses of cobalt blue glass should be interposed between the flame and the eye to absorb the yellow light produced by sodium.

SUMMARY

Sodium and **potassium** are made by the electrolysis of their hydroxides.

	Atomic Wt.	Specific Gr.	Melting Pt.	Boiling Pt.
Sodium	23.0	.97	97.6°	877°
Potassium	39.1	.87	62.5°	757°

Both **metals** are soft and light. They react with water to form hydroxides, and with acids to form salts.

Their **compounds** are characterized by the colors they impart to a non-luminous flame. Most of the compounds are colorless (white when powdered), and soluble in water, the potassium compounds being more soluble.

The **hydroxides** of sodium and potassium are typical bases — caustic, alkaline, and neutralizing acids. They are used in the preparation of soaps and bleaching solutions, in oil-refining, and in glass-making.

EXERCISES

1. Why was the preparation of metallic sodium a difficult chemical problem to solve?

2. Does melted sodium hydroxide act on iron and nickel? Give a reason for your answer.

3. Why cannot a water solution of sodium hydroxide be used for the electrolytic preparation of sodium?

4. Sketch the apparatus for making sodium. Label each part. What are the uses of the wire gauze? What goes to the cathode? To the anode?

5. Compare the properties of sodium with the corresponding properties of metals with which you are more familiar, for example, iron, copper, silver. Do you find any resemblances?

6. Why is sodium classed as a metal?

7. What are the most essential properties of metals from the chemical point of view?

8. Why does neither sodium nor potassium occur in an uncombined state in nature?

9. How may sodium be kept? Explain.

10. What properties of sodium prevent its use as an electric conductor?

11. Calculate the quantity of sodium that could be obtained from 1 kilogram of pure sodium hydroxide.

12. Why would it be extremely dangerous to drop into water a large piece of sodium or potassium?

13. Write the equation for the reaction of potassium with water. What would be obtained if the resulting solution were evaporated to dryness?

14. Calculate the quantity of sodium hydroxide that would be formed by the action of 5 grams of sodium on water. What weight of hydrogen would be evolved? What volume would the hydrogen have under standard conditions?

15. Is potassium hydroxide a base? Why?

16. What is neutralization?

17. What weight of hydrogen chloride would be required for the complete neutralization of 2.63 grams of sodium hydroxide?

18. What right have we to believe that many of the terrestrial elements exist in the sun?

19. Mention two methods for preparing hydrogen from water.

CHAPTER XVI

SOLUTION[1]

We have found that many of the reactions studied take place only in the presence of water, even though the water itself does not react.

140. Conducting Power of Solutions. — We have already seen that water solutions of sodium chloride and sulphuric acid (electrolysis of water) readily permit the passage of the current. Solutions differ from each other greatly in their power to conduct electricity. We may test other solutions by arranging a circuit that includes a source of current, the substance to be tested, and some instrument to detect the passage of the current, as an incandescent lamp, in series. In Fig. 38 is a beaker (*a*) containing the solution to be tested, and *b*, *b* are electrodes with mercury contacts.

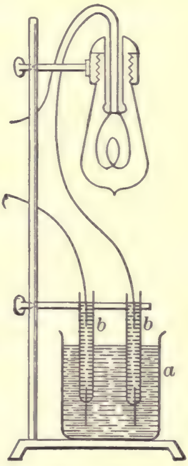


Fig. 38. — Determination of Electrolytes.

The incandescent lamp serves two purposes. Its resistance cuts down the current to a strength suitable for passing through a solution. Secondly, if the lamp lights, the current must be passing through

[1] Note to Instructor. — Although this and the following chapter may be taken up at this point, many instructors prefer to postpone their discussion until the students have become acquainted with a wider range of chemical phenomena.

the liquid in the circuit, and the solution is a conductor. The brilliancy with which the lamp glows roughly indicates how well the solution in the circuit conducts.

When distilled water is put into the circuit, the lamp does not even glow; hence, in those water solutions which are conductors, the current must be carried by the aid of the dissolved substance. A water-solution of hydrochloric acid conducts the current readily; a solution of sugar fails to conduct, but a solution of sodium hydroxide, a typical base, proves as good a conductor as hydrochloric acid. Solutions of sulphuric acid, potassium hydroxide, sodium chloride, sodium sulphate, and copper sulphate all allow the lamp to glow brilliantly. When a solution of acetic acid is tested, the lamp barely glows. Glycerine, alcohol, and many similar compounds are found to be non-conductors.

141. Electrolytes and Non-electrolytes. — Our circuit includes two different classes of conductors. The first consists of solid conductors, chiefly metallic, such as the copper wire and the carbon filament of the lamp. These conductors undergo no permanent change in carrying the current. The other class includes those liquids that we have found to be conductors, the components of which are free to move toward the electrodes, which are the places where the current enters and leaves the liquid. In these liquid conductors, the transmission of electricity is attended by the decomposition of the solute, components of which may be liberated at the electrodes. A liquid that is permanently decomposed during the passage of an electric current is called an *electrolyte*. The name given to the process is *electrolysis*.

Arranging the electrolytes and non-electrolytes in two columns, we obtain results similar to those indicated in the table:

Electrolytes	Non-electrolytes
hydrochloric acid	distilled water
sulphuric acid	
sodium hydroxide	sugar
potassium hydroxide	
sodium chloride	glycerine
sodium sulphate	
copper sulphate	alcohol

An examination of the column of electrolytes shows that it contains only acids, bases, and salts. All electrolytes belong to these classes of compounds. The non-electrolytes in the second column are not generally placed in any of these classes of compounds. Why is it that water solutions of acids, bases, and salts conduct electricity, while other substances fail? This question has led to a more careful study of the properties of water solutions.

142. Effect of Dissolved Solids on the Freezing Point.— Under ordinary conditions of pressure pure water freezes at 0° C. and boils at 100° C. The addition of any soluble solid lowers the freezing point and raises the boiling point. We shall discuss only the freezing point. All water solutions freeze at a lower temperature than pure water. Careful measurements show that the amount of the lowering depends on the mass of the substance added. A solution containing 10 grams of sugar to one liter of water will freeze at a point twice as far below 0° as one containing 5 grams of sugar to 1 liter of water. According to the atomic theory 10 grams of sugar contain twice as many molecules as 5 grams. Therefore, the lowering of the freezing point of the pure solvent is proportional to the number of sugar molecules dissolved.

The depression of the freezing point of water (Fig. 39)[1] produced by equal numbers of molecules of different substances has been carefully determined. To get equal numbers of molecules, a weight in grams equal to the molecular weight of each substance was dissolved in 1 liter of water. Thus 46 grams of alcohol, C_2H_5OH, and 342 grams of sugar, $C_{12}H_{22}O_{11}$, were each dissolved in a liter of water. In both cases the resulting solutions froze at $-1.86°$. It was further found that a solution of any non-electrolyte containing a gram-molecular weight of the solute to the liter gave this same lowering of the freezing point. If weights of non-electrolytes proportional to their molecular weights are dissolved in equal volumes of the same solvent, the solutions will freeze at the same temperature. This is strictly true for dilute solutions only. This indicates that the depression of the freezing point is dependent on the *number* of molecules present and not on the weight or kind of these molecules. But if common salt is used, we find that, in dilute solution, the freezing point is lowered nearly twice as much as in the case of a solution of a non-electrolyte containing the same number of molecules. This can be explained by as-

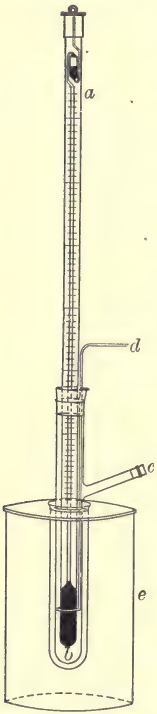


FIG. 39.

[1] Figure 39 represents an apparatus for determining the depression of the freezing point. A Beckmann thermometer (a) is used and the liquid to be frozen is held in the inner tube (b). Through the side tube (c) is introduced the substance whose effect on the freezing point of the pure solvent is to be determined. A stirring rod (d) moves up and down in the solution, which is cooled by a freezing mixture contained in the outer vessel (e).

suming the presence of *twice as many particles* in a solution containing a molecular weight of salt as in the same volume of a solution containing a molecular weight of sugar. In other words, we have reason to think that when they are dissolved in water, all or nearly all of the salt molecules are separated, each into two particles. Other electrolytes behave as salt does, while non-electrolytes act like sugar.

143. Osmotic Pressure. — The effect of solutes in raising the boiling points and lowering the freezing points of solvents is closely connected with what is called *osmotic pressure.* A crystal of copper sulphate placed at the bottom of a tall cylinder of water will finally distribute itself uniformly throughout the liquid. A considerable weight of the copper sulphate thus rises in spite of the attraction of gravitation, indicating that a pressure is at work.

It is believed that the particles of copper sulphate move at high velocities as they leave the crystal. They travel in straight lines until they strike other particles or one of the surfaces that inclose the liquid, when they rebound, still moving at high velocities. In other words, the dissolved particles are believed to act like the molecules of a gas, and a pressure is produced, just as it is in a gas, by the impacts of the moving particles. This is known as osmotic pressure.

144. Measurement of Osmotic Pressures. — This is accomplished by the use of cells that contain within their walls membranes through which water, but not the solute, can pass (Fig. 40). These are called semi-permeable membranes. The osmotic pressure in even a fairly dilute solution is enormous. The solution therefore tends to

expand, and so to become more dilute. This possibility exists if the solution is contained in a semi-permeable cell which is surrounded by water. The water will enter, diluting the solution until a water pressure is produced that equals the osmotic pressure.

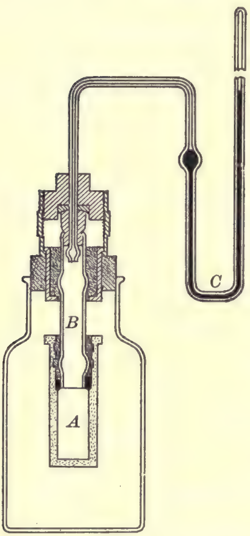


FIG. 40. — OSMOTIC CELL. *A*, semi-permeable cell; *B*, glass connecting tube; *C*, mercury gauge to show pressure produced.

145. Analogy between Osmotic Pressure and Gas Pressure. — Osmotic pressures, like gas pressures, are found to depend on the number and not on the kind of particles that cause them. Boyle's and Charles' Laws apply also to osmotic pressures. A statement analogous to Avogadro's Hypothesis can be made concerning the number of dissolved particles in equal volumes of solutions at equal temperatures and equal osmotic pressures. In fact, the solute, in producing this pressure, acts as if it were a gas confined within a volume equal to that of the solvent.

146. Dissociation of Electrolytes. — A careful study of the boiling point shows a greater elevation in the case of electrolytes than in non-electrolytes, in proportion to the number of dissolved molecules. The differences in the freezing point and boiling point, produced by equal numbers of molecules of electrolytes and non-electrolytes, may all be explained by assuming that in electrolytes the dissolved molecules are broken up or *dissociated* into parts as soon as they are dissolved. In non-electro-

Michael Faraday (1791–1867), the son of a blacksmith, was born in a suburb of London. At the age of fourteen he was apprenticed to a bookbinder, but devoted his spare time to reading and attending lectures on physical science. He heard Davy lecture at the Royal Institution and wrote him, expressing a desire to enter the service of science. He became Davy's laboratory assistant in 1813. Faraday sacrificed much in order to devote his time to pure science, and his discoveries are numerous, including benzene, magneto-electric induction, electrochemical equivalents, and the liquefaction of several gases. He expressed the belief that gases are liquids having a very low boiling point.

lytes the molecules of the dissolved substance are not dissociated.

147. Chemical Activity of Electrolytes. — We have already noted the fact that acids, bases, and salts are electrolytes; these are the substances that we have made use of in the greater part of our chemical actions so far. Nearly all chemical actions require the presence of water. When two solutions of electrolytes are mixed, action takes place rapidly if one of the products of the reaction is either insoluble or gaseous. So we may say that in general electrolytes are very active chemically. Non-electrolytes, on the other hand, usually show very little activity.

148. Ions. — To the moving particles that are formed in the electrolyte while solution is taking place Faraday gave the name *ions*, meaning wanderers. We have just seen that the hydrochloric acid molecule is broken up, *in the act of dissolving*, into two particles; these must be the hydrogen and chlorine atoms. Why do they move in opposite directions? Bodies with electrical charges of opposite kind attract each other. Since the hydrogen particles in a water solution are attracted toward the cathode, or negative pole, these hydrogen particles must be positively charged. Similarly the chlorine particles must have negative charges, since they are drawn toward the positive pole or anode.

When a solution of copper sulphate is electrolyzed, copper appears at the cathode and experimental evidence shows the presence of combined sulphur and oxygen at the anode. The copper sulphate must therefore dissociate while dissolving into Cu, a positive (+) ion, and SO_4, a negative (−) ion. *An ion, then, is an atom or group of atoms carrying an electric charge.*

149. Osmotic Pressures as a Proof of Ionization. — In solutions of electrolytes we find abnormally high osmotic pressures. If the substance is one that, like hydrogen chloride, gives only two ions, the pressure will be twice that of a similar solution of a non-electrolyte. This is what we would expect from the theory of ionization, and the agreement constitutes a striking proof of the theory.

150. Explanation of Electrolysis. — Sodium chloride dissociates in water into sodium and chlorine ions. From the intensity with which sodium ordinarily reacts with water, we might expect the instant formation of sodium hydroxide. But this cannot be present, for the solution is perfectly neutral in reaction. The sodium *ion* does not react with water. But when a current is passed through a solution, the positive charges of the sodium ions are neutralized by contact with the negative electrification of the cathode; the sodium ions then become sodium *atoms* and react with the water surrounding the cathode, forming sodium hydroxide. It should be understood, however, that *the electric current is not the cause of the dissociation into charged particles, but simply determines the direction in which they move.* The dissociation took place while the substance was dissolving.

The chlorine ions give up their negative charges the instant they touch the anode, neutralizing in part the positive charge on that electrode. The particles of chlorine without their charges are ordinary atoms, which unite in pairs to form molecules of chlorine gas, which bubbles off at the anode.

151. Differences between Ion and Atom. — Ions should not be confused with atoms. The existence of an electric charge on an atom entirely changes its properties, as may

be seen from the electrolysis of sodium chloride just described. Atoms of chlorine tend to combine in pairs to form molecules of green chlorine gas; ions of chlorine are colorless and repel each other because they possess like charges.

The differences between ion and atom may now be stated as follows: first, an ion has an electric charge, an atom has not; second, a single ion often includes several atoms of different elements.

152. Ionization of Acids and Bases. — When an electrolyte is dissolved in water, some of its molecules enter the solution undissociated, while the other molecules separate into particles which become electrically charged in the process. On passing the current through a solution of hydrochloric acid, we find hydrogen collecting at the cathode and chlorine at the anode. In the solution there must be positively charged hydrogen ions and negatively charged chlorine ions. The electrolysis of nitric acid reveals the presence of hydrogen ions and NO_3 ions; that of sulphuric acid shows two hydrogen ions and one SO_4 ion for each molecule dissociated. The electrolysis of other acids gives, in every case, hydrogen at the cathode and so indicates the presence of hydrogen ions. To these are ascribed the characteristic properties of acids. This hydrogen ion, common to all acids, is responsible for the sour taste, and for turning litmus red. The presence of hydrogen in a compound does not make it an acid; the compound must give hydrogen ions in water solution. Liquefied hydrogen chloride, free from water, fails to act as an acid, because none of its molecules break up so as to give hydrogen ions. *An acid is a hydrogen compound whose water solution contains hydrogen ions.*

When bases are dissolved in water, the metallic atom in the molecule becomes the positive ion and the hydroxyl

group the negative ion. The hydroxyl ions are the only ions common to all bases, and to them the characteristic properties of bases are attributed. Hence the definition: *A base is a hydroxide whose water solution contains hydroxyl ions.*

153. Effect of Dilution on Ionization. — It will be readily seen that the more ions there are present in a given solution, the better it will conduct the current, for the ions act as carriers. So we can measure the degree of ionization by the conducting power of the solution, provided there is the same weight of solute between the electrodes in every case. Conductivity under these conditions is called molecular conductivity. We find, as we continue to dilute an electrolyte, that the molecular conductivity increases up to a certain point, beyond which it does not change. This might be expected, for at a certain dilution all the molecules are dissociated, and a furthur dilution causes no further dissociation. The effect of dilution on ionization is shown in the following table, in which m is the number of gram molecules in 1000 grams of water. The numbers give the relative conductivity.

m	HNO_3	HCl	KCl	NaCl
1.00	2770	2780	919	695
0.50	2991	3017	958	757
0.10	3225	3244	1047	865
0.05	3289	3330	1083	897
0.01	3395	3416	1147	962

154. Activity of Acids and Bases. — The chemical activity of an acid depends upon the extent to which its dissolved molecules are dissociated into ions. Hydrochloric acid is almost wholly dissociated into its ions in dilute solution.

Svante August Arrhenius was born at Wijk, Sweden, in 1859. He is the present director of the Physico-chemical Department of the Nobel Institute. His great work was the invention in 1887 of the modern theory of dissociation in electrolytes, commonly known as the ionization hypothesis. This conception has done much to bind into an orderly system many previously unexplained experimental observations.

Jacobus Henricus van't Hoff (1852–1911) was born at Rotterdam, Holland. He become Professor of Physical Chemistry to the University of Berlin in 1894. He possessed great depth of scientific imagination and will be remembered for his brilliant work in developing several of the generalizations of modern physical chemistry and for the application of physical chemistry to geology.

This is why it acts vigorously on metals and neutralizes bases. Such an acid is spoken of as a ***strong acid.*** Nitric acid is another example of a strong acid. Sulphuric acid, which is dissociated but two thirds as much as the acids just mentioned, is not so strong an acid. Acetic acid is the type of a weak acid, because it is so slightly dissociated (less than 2% in dilute solution) that it does not act vigorously on most metals, and its reactions with other substances are slow.

The term *strength of acid* must not be confused with the term *concentrated acid.* Concentrated sulphuric acid usually contains about 95% H_2SO_4, while concentrated hydrochloric contains but 37% HCl. Sulphuric acid, then, is usually the more concentrated, but it is the weaker acid of the two. Hydrochloric acid is the more reactive, since it is dissociated to a greater extent in water solution. In the preparation of hydrogen chloride, the reason for the displacement of hydrochloric acid by sulphuric acid is not that sulphuric acid is a stronger acid, but that it has a higher boiling point.

As in the case of acids, the strength of a base depends upon the degree of ionization it undergoes in solution. Sodium hydroxide and potassium hydroxide are almost completely dissociated in dilute solutions. They are types of strong bases.

155. Explanation of Neutralization. — When we mix dilute solutions of hydrochloric acid and sodium hydroxide, we have present in the mixture positive ions, hydrogen and sodium, and negative ions, chlorine and hydroxyl. Each positive hydrogen ion will attract a negative hydroxyl ion, and *vice versa.* The two ions combine, the equal opposite charges neutralize each other, and a molecule of undissociated water results. Indicating the sign of the charge

by a + or − above and to the right of the symbol, we may express this charge by the equation:

$$H^+ + OH^- \longrightarrow H_2O$$

As the water formed is practically undissociated (only two molecules in a billion), we may consider it as completely removed from the action as if it had formed an insoluble compound or precipitate. In the neutralization, for each H^+ ion withdrawn in this way a Cl^- ion is left, and for each OH^- ion a Na^+ ion remains. These will not unite permanently so long as water is present, for the sodium chloride is dissociated as fast as it is formed. The neutralization is complete, when there are neither H^+ nor OH^- ions left to give an acid or a basic reaction, and the solution then contains equal numbers of Na^+ and Cl^- ions. The equation showing these facts is:

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow H_2O + Na^+ + Cl^-$$

If the solution is now concentrated, the degree of dissociation is lessened, and Na^+ and Cl^- ions will unite to form undissociated sodium chloride. When evaporation is complete, we find that they have completely united, forming crystals of salt.

156. Products of Neutralization. — We get similar results from the use of other acids and bases. Potassium hydroxide and hydrochloric acid give *water*, K^+ ions and Cl^- ions. Nitric acid and sodium hydroxide yield undissociated water, Na^+ ions and NO_3^- ions.

$$K^+ + OH^- + H^+ + Cl^- \longrightarrow H_2O + K^+ + Cl^-$$
$$Na^+ + OH^- + H^+ + NO_3^- \longrightarrow H_2O + Na^+ + NO_3^-$$

In every case of neutralization the products are:

(1) undissociated water;
(2) a solution containing positive ions from the base and negative ions from the acid;
(3) energy in the form of heat.

During the evaporation of the solvent the positive ions from the base unite with the negative ions from the acid to form a compound known as a *salt.*

157. Heat of Neutralization.—Neutralization, as a chemical process, is essentially the formation of undissociated water molecules. It is always accompanied by the liberation of heat. When dilute solutions, containing equal amounts of a strong acid, are neutralized by different strong bases, the same quantity of heat is produced in each case. This heat is known as the *heat of neutralization.*

Table showing heat of neutralization expressed in calories, using gram-molecular weights:

	HCl	HNO_3
$NaOH$	13,700 cal.	13,700 cal.
KOH	13,700 cal.	13,700 cal.

This uniformity in the heat of neutralization indicates that the action is the same in all these cases. The only common product is water. *Therefore, the heat of neutralization is the heat evolved by the formation of water from hydrogen and hydroxyl ions.*

158. Charges carried by Ions. — We have seen that one molecule of hydrochloric acid neutralizes one molecule of sodium hydroxide, producing one molecule of water. But we find that to neutralize one molecule of barium hydroxide, $Ba(OH)_2$, two molecules of hydrochloric acid are required, according to the equation:

$$Ba(OH)_2 + 2\ HCl \longrightarrow 2\ H_2O + BaCl_2$$

The barium chloride is largely dissociated into barium and chlorine ions. In any solution, the positive charges must equal the negative charges. Therefore, in this case each barium ion must contain two positive charges to equal the negative charges on the two chlorine ions. Sulphuric acid dissociates into H^+, H^+, and SO_4^{--} ions; the SO_4^{--} ion must carry two negative charges to balance the positive charges of the two hydrogen ions.

$$H_2SO_4 \rightleftarrows H^+ + H^+ + SO_4^{--}$$

Some other ions carry three and even four charges.

No. of Charges	Positive Ions	Negative Ions
1	H, Na, K, Li, Ag, NH_4,	OH, F, Cl, Br, I, NO_3, ClO_3, and other negative ions of monobasic acids
2	Ca, Sr, Ba, Mg, Zn, Hg, Co, Ni, Cu (cupric), Fe (ferrous), Sn (stannous)	S, SO_4, CO_3, and other negative ions of dibasic acids
3	Al, Bi, Sb, Fe (ferric)	PO_4 and other negative ions of tribasic acids
4	Sn (stannic)	SiO_4 and negative ions of tetrabasic acids

The preceding table shows the common ions with the number of charges carried by each and the signs of the charges.

159. Valence of Ions. — Atoms differ with respect to the number of atoms of other elements with which they combine. We have defined this as valence (§ 111).

In electrolytes, the valence of each ion is numerically equal to the number of charges carried by it. This, of

course, does not *explain* the valence of atoms in non-electrolytes, but does indicate a connection between the valence and the electrical capacity of an atom in an electrolyte.

160. Ionization in Other than Water Solution. — While ionization takes place to a higher degree in water than in other solvents, it seems certain that the separation takes place to at least a small extent in every case of solution. The power of a solvent to cause ionization depends on several of its properties, an important one being the degree to which the substance limits the force of attraction between positively and negatively charged bodies. Water does this to a considerable degree, hence there is much tendency for ions to remain apart in water solution. Methyl alcohol offers less hindrance to the attraction, and we find, as the theory indicates, that methyl alcohol is only a fairly good ionizing solvent. Benzene offers very little hindrance, and, as we would expect, there is almost no ionization in this medium.

Fused salts, even in the complete absence of water, often conduct an electric current. This indicates ionization.

With the careful study that has followed the development of the hypothesis of ionization, chemists have come to believe that in the great majority of cases chemical action occurs between ions and not between molecules. With the aid of this theory many things not previously understood have been fully explained.

SUMMARY

Solutions are classified as **electrolytes** and **non-electrolytes**, according to their conducting power. The electrolytes include solutions of acids, bases, and salts.

The **effect of dissolved substances** on the boiling point, freezing point, and osmotic pressure indicates that the molecules of the solute are dissociated in the case of electrolytes. Electrolytes are more active chemically than non-electrolytes.

The portions into which a molecule dissociates are **ions** and carry equal and opposite electric charges. When an electric current is passed through an electrolyte, each ion passes to the electrode of opposite sign and is there discharged and liberated. **Acids** furnish **hydrogen ions** in solution; **bases** furnish **hydroxyl ions**, and **salts** furnish **other ions.** The percentage of ionization increases with the dilution until ionization is complete.

The **strong** or **active acids and bases** are those which are highly dissociated. The essential action in **neutralization** is the union of the hydrogen and hydroxyl ions to form undissociated water; during the evaporation, the union of the other ions to form a salt is completed. The strong acids and bases unite with the same heat of neutralization for equivalent quantities.

Hydrogen and metallic ions carry positive charges; the nonmetallic ions, negative charges. The **valence** of an ion is numerically equal to the number of charges carried by it.

EXERCISES

1. State and explain on the basis of the theory of electrolytic dissociation, what happens when a current of electricity is passed through a solution of sodium chloride.

2. How do you determine whether a given solution is an electrolyte?

3. When a beaker of acetic acid is put in circuit with an incandescent lamp, the lamp glows feebly, while the solution of sodium acetate allows it to glow brightly. What does this show?

4. Compare the freezing point of sea water with that of ordinary rain water.

5. Why will substances often react with each other in solution while they will not in a dry state ?

6. What ions are present in solutions of the following: KCl, $ZnSO_4$, $KClO_3$, NaOH ?

7. Distinguish carefully between an ion of potassium and an atom of potassium.

8. What element is common to all acids ? What group of elements is common to all bases ? Select an acid and a base and by an equation show that you understand the meaning of the term neutralization.

9. Show two essential differences between a solution of salt in water and the suspension of an insoluble powder in water.

10. Why is nitric acid a more active acid than sulphuric acid ?

11. Give the changes that take place and the products formed in the following cases:

(*a*) when nitric acid is added to water;

(*b*) when a piece of caustic potash is dissolved in water;

(*c*) when the two solutions are mixed.

12. A piece of red litmus turns blue in a solution of sodium carbonate (Na_2CO_3). Name the ions shown to be present by this test.

13. Write equations, indicating ions, for the neutralization of potassium hydroxide with sulphuric acid; of nitric acid with ammonium hydroxide.

CHAPTER XVII

CHEMICAL EQUILIBRIUM

161. Reversible Reactions. — We have already had occasion to point out that some chemical actions "work backwards." For example, we may write the equation:

$$3\,Fe + 4\,H_2O \rightleftarrows Fe_3O_4 + 8\,H$$

This reaction goes one way or the other according to the conditions that we establish. If we keep a current of steam passing over hot iron, it proceeds from left to right; if we pass hydrogen over hot iron oxide, it goes from right to left.

Ionizations are also excellent examples of reversible action:

$$NaCl \leftrightarrows Na^+ + Cl^-$$

If we dissolve salt in water, the action goes to the right; if we evaporate water from the solution, the action goes to the left.

162. Dynamic Equilibrium. — In a solution of sodium chloride, provided it is not extremely dilute, we always find molecules as well as the two kinds of ions. The ratio between the dissociated and the undissociated molecules does not change so long as the volume of the solution and its temperature remain constant. In other words, a condition of equilibrium exists. But there are many reasons for believing that this is not a motionless

equilibrium. On the contrary, it is supposed that both the reactions indicated in the above equation are constantly taking place, and that the condition of equilibrium results because the action is proceeding just as fast one way as the other. Thus we have a balanced condition. This is described as *dynamic* (*i.e.* moving) *equilibrium.*

Consider again the action between copper and water. The two constituents are heated in a *sealed* glass tube. Under this condition no substance can escape. Consequently, after a little hydrogen and copper oxide have been formed, they immediately begin to act on each other, independently of the action which produced them, producing copper and water again. In the beginning the direct action proceeds with the greater speed; but the reverse action gradually gains, until finally they are going with equal speeds, thus balancing each other, so that the action *seems* to stop. Now if we seal equivalent quantities of copper oxide and hydrogen in a second tube and heat them, we arrive at exactly the same result as in the first tube; that is, we have all four substances, copper, copper oxide, water, and hydrogen, and we have them in the same proportion as in the first tube. This fact tends to confirm our belief that the equilibrium reached is dynamic in character.

This conception also explains the condition that exists in many cases where, on mixing two substances, no action seems to occur, but in which reactions are actually going on. For example, sodium chloride and potassium nitrate are dissolved in the same solution. Apparently there is no action, but actually there are several cases of equilibrium. At first we have those resulting from the ionization of the two salts:

$$NaCl \rightleftarrows Na^+ + Cl^-$$
$$KNO_3 \rightleftarrows K^+ + NO_3^-$$

Then K^+ ions will join with Cl^- ions, giving a new equilibrium:

$$K^+ + Cl^- \rightleftarrows KCl$$

and Na^+ with NO_3^- will give another:

$$Na^+ + NO_3^- \rightleftarrows NaNO_3$$

Thus we have in such a solution eight different things present at any instant, and four cases of dynamic equilibrium.

We must note, however, that in this case, as with the sealed tubes, *no product can escape from the field of action.* In cases where one of the products does escape, there can be no reverse action, since some of the necessary constituents are lacking.

163. Reactions that go to an End. — If, in the case of the reactions of copper with water, the tubes had been open, either the steam or the hydrogen would have escaped from the field of action before it could have reacted in the reverse direction. This is what happens if we reduce copper oxide by passing hydrogen over it, or if we pass steam through a tube containing copper. In these cases the reactions continue in one direction until one or both of the constituents have been entirely converted into products; such an action is said to *go to an end.*

Usually in practical chemical work we desire that our actions shall continue until we obtain as much of the product as possible. In selecting and controlling such actions, the modern theories of reversibility, equilibrium, and the effect of concentration are of great value.

164. Reactions that go to an End through Volatility. — If, at the temperature of the experiment, one of the products

of an action is a gas, it will readily escape from the reacting mixture. The preparation of hydrogen chloride is an excellent example of an action that goes to completion in this way:

$$2\,NaCl + H_2SO_4 \longrightarrow 2\,HCl + Na_2SO_4$$

Sulphuric acid is chosen for the reason that its boiling point is so high that there is no possibility of its leaving the mixture at the temperature which will suffice to drive off the hydrogen chloride.

This principle of *volatility* is of practical use in preparing chemical compounds. If the substance we desire is not itself volatile, we may still employ the principle by selecting our constituents so that another product will be volatile.

165. Reactions that go to an End through Insolubility. — We have seen that solution must precede ionization. An insoluble substance does not, therefore, yield ions, even though it may be floating in the solvent. Hence, if an insoluble substance is formed in a solvent as the result of a reaction, it is as much out of the field of action as if it had left the mixture. Reactions in which this happens go to an end just as they do if a volatile product is formed. This is one of the most common types of chemical action. As an example, consider the action between solutions of silver nitrate and sodium chloride:

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

Silver chloride is insoluble in water. It therefore forms no ions, and is out of the field of action when once formed. Obviously it cannot play any part in causing a reverse action.

166. Reactions that go to an End through Non-Ionization. — This resembles the preceding case. A substance may form which, although soluble, does not ionize. As far as causing a reverse action is concerned, this substance is out of the field of action.

That neutralization actions go to an end is due to this fact. The water, which is invariably formed, is practically non-ionized.

167. Insoluble Substances used as Tests. — The test for hydrochloric acid or a chloride is a search for the presence of chlorine ions. The solution of silver nitrate used in the test contains silver ions:

$$AgNO_3 \rightleftarrows Ag^+ + NO_3^-$$

These positive silver ions will encounter negative chlorine ions if the solution tested contains a chloride. Silver chloride is formed. This compound, being practically insoluble and hence undissociated, separates as a precipitate. Therefore the equation is:

$$Ag^+ + Cl^- \longrightarrow AgCl$$

A solution of potassium chlorate also contains chlorine, not as a simple ion, but as part of the ion ClO_3^-. So when we mix this solution with the silver nitrate, we have the ions Ag^+, NO_3^-, K^+, ClO_3^-. Here no precipitation takes place, since the compounds, silver chlorate, $AgClO_3$, and potassium nitrate, KNO_3, that would be likely to form, are both soluble. Silver nitrate solution, then, is the test for the chlorine *ion*, and not for the chlorine *atom*.

The test for a sulphate depends upon the combination of barium ions, Ba^{++} (from the barium chloride added), with the SO_4^{--} ion of the sulphate. The barium sul-

phate formed is insoluble and separates as undissociated molecules. The equation is:

$$Ba^{++} + SO_4^{--} \longrightarrow BaSO_4$$

These tests furnish good examples of reactions that go to an end through insolubility.

168. Law of Mass Action. — The theory of moving particles, which we used to explain osmotic pressure, can also be employed to make clear some matters connected with ionization and equilibrium. In a solution, both ions and molecules are in constant movement, and there are constant collisions between the particles. As a result, some gain momentum while others lose it, until finally the particles have widely different velocities. In a case where there exists a dynamic equilibrium like that shown in the equation

$$NaCl \rightleftarrows Na^+ + Cl^-$$

the reactions in the two directions are affected by the nature of the collisions which occur. If a molecule of sodium chloride meets with a violent impact, it will tend to separate into its ions; while two oppositely charged ions may meet in such a way as to remain united. Thus the reactions in the two different directions are accounted for.

Next we will consider an experiment. To a saturated solution of common salt we add hydrogen chloride gas. This in dissolving tends to reach the equilibrium:

$$HCl \leftrightarrows H^+ + Cl^-$$

It thus gives ions of a kind already in solution. In other words, we increase the *concentration* of the chlorine ions. As an experimental result of the addition, we observe

that sodium chloride is precipitated in the form of fine crystals.

The following is the explanation of this action. By increasing the number of chlorine ions in the solution, we increase the number of impacts between the Na^+ and Cl^- ions and consequently the chance of forming more sodium chloride molecules. Since the solution is already saturated with these, the newly formed ones must precipitate. A similar result may be obtained if we add a substance, like sodium nitrate, which would increase the concentration of the Na^+ ions. Thus, in general, we can increase the speed of a chemical action by increasing the impacts between the substances which produce the action. This occurs when the concentration of even one of the substances is increased; and in these cases the action goes further toward completion.

The law which states these generalizations is known as the *Law of Mass Action.* In its full form it gives the mathematical relations of the concentrations, but for our purposes we can put it in thus: *The speed of a chemical action is increased in a given direction by increasing the concentration of one of the substances that produce the action.*

169. Applications of the Law of Mass Action. — These are of very great importance, since the principle, like those involved in ionization and equilibrium, is of general application. Chemical actions which go to an end are themselves examples of the operation of the law. When a substance leaves the field of action through its insolubility, volatility, or non-ionization, the concentration of that substance becomes zero, and there can be no impacts between it and another substance tending to produce a reverse action.

But most actions do not go to an end. Control in such

cases is often secured through a knowledge of the principle of mass action. Perhaps the most important examples are those involving a substance that is almost, but not wholly, insoluble. Barium sulphate is a compound of this kind. Therefore the reaction

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl$$

goes only approximately to an end. But it is often necessary to precipitate barium as a sulphate as completely as possible. The principle of mass action points a way to accomplish this, by the addition of a considerable excess of sulphuric acid when producing the precipitation. The concentration of the SO_4^{--} ions is thereby increased, and the Ba^{++} ions are brought almost completely into reaction.

Again, the activity of an acid can be greatly lessened by the addition of a salt of the acid. For example, if to the equilibrium:

$$H_2SO_4 \rightleftarrows H^+ + H^+ + SO_4^{--}$$

we add sodium sulphate:

$$Na_2SO_4 \rightleftarrows Na^+ + Na^+ + SO_4$$

we thus increase the concentration of the sulphate ions, and some of the hydrogen ions are forced back into molecules of sulphuric acid. Since acid properties are due to hydrogen ions, the acid strength of the solution in question is lessened by the addition of the sodium sulphate. In an analogous way, a weak acid becomes practically inactive in the presence of its own salts. This is especially true because the salts of weak acids are much more highly ionized than the acids themselves.

SUMMARY

Chemical actions in general are **reversible.** Hence, unless special conditions are established, two substances do not give complete reaction with each other on being mixed. A reversal action sets in, and both it and the direct action continue simultaneously. A state of **dynamic equilibrium** thus exists.

Where reactions do not remain in a state of dynamic equilibrium but do **go to an end**, it is because one of the products **leaves the field of action.**

This may happen through **insolubility, volatility,** or **non-ionization.**

The reactions of the laboratory are chosen so that they will **go to an end** through the operation of one of these principles.

Tests for chlorides, sulphates, and other ions are good examples of action that go to an end through **insolubility.**

The preparation of hydrogen chloride is a good example of an action that goes to an end through **volatility.**

Neutralizations go to an end because the water that is formed is practically **non-ionized.**

The character of the equilibrium in a given chemical action can be controlled through the **Law of Mass Action**, which states: **The speed of a chemical reaction is increased in a given direction by increasing the concentration of one of the substances that produce the action.**

Examples of the practical application of the law of mass action are found in the facts that (*a*) a partly soluble substance can be almost completely precipitated by adding an excess of one of the ions that help to form it, and (*b*) that acids are less active in the presence of their own salts; this is especially true in the case of weak acids, because the salts of these acids are generally much more highly ionized than the acids themselves.

EXERCISES

1. What is meant by reversible reactions? Give three examples.

2. Explain the meaning of the word dynamic in the phrase *dynamic equilibrium.*

3. Write an equation to show that the ionization of potassium nitrate is a reversible reaction. Under what conditions can the speed be increased reading from left to right? From right to left?

4. Write an equation to show the ionization of copper sulphate in water solution. Does this represent an action that goes to an end? Explain.

5. Under what three conditions do actions go to an end? Explain.

6. By reference to the Table and Rules for Solubility and Volatility in the Appendix, determine which of the following reactions go to an end, and which rest in a state of equilibrium. State the reason in each case, and complete the equation in case the reaction goes to an end:

$HgNO_3 + KCl \longrightarrow$	$Na_2SO_3 + H_2SO_4 \longrightarrow$
$CuSO_4 + NaNO_3 \longrightarrow$	$Pb(NO_3)_2 + Na_2SO_4 \longrightarrow$
$Na_2CO_3 + HNO_3 \longrightarrow$	$NH_4Cl + NaOH \longrightarrow$
$NaBr + H_2SO_4 \longrightarrow$	$Zn(NO_3)_2 + H_2SO_4 \longrightarrow$
$BaCl_2 + CuSO_4 \longrightarrow$	$FeCl_3 + K_2SO_4 \longrightarrow$
$ZnS + H_2SO_4 \longrightarrow$	$Pb(NO_3)_2 + CuCl_2 \longrightarrow$
$Na_2SO_4 + HCl \longrightarrow$	$FeS + H_2SO_4 \longrightarrow$
$NaOH + HNO_3 \longrightarrow$	$NaNO_3 + HCl \longrightarrow$
$KNO_3 + Na_2SO_4 \longrightarrow$	$AgNO_3 + FeCl_3 \longrightarrow$
$CaCl_2 + Na_2CO_3 \longrightarrow$	$CaCO_3 + HCl \longrightarrow$

7. Write equations to show three ways of making potassium nitrate, illustrating each of the three ways in which reactions may go to an end.

8. State the Law of Mass Action.

9. Lead sulphate is slightly soluble in water. What could be added to make it less soluble? Explain.

10. Is common salt as soluble in a dilute solution of hydrochloric acid as it is in water? Explain.

11. Which is the more ionized in water solution, a weak acid or its sodium salt?

12. If sodium acetate is present in a solution of acetic acid, what is the effect on the activity of the acid?

13. Why does the zinc in a hydrogen generator dissolve less rapidly after a time, even though there is still an excess of sulphuric acid present?

14. Hydrogen and the magnetic oxide of iron react according to the reversible equation:

$$Fe_3O_4 + 4\,H_2 \rightleftarrows 3\,Fe + 4\,H_2O$$

How may the direction of the reaction be controlled? How may dynamic equilibrium be established?

15. Calcium sulphate is but slightly soluble in water. Why is it difficult to dissolve much calcium carbonate in dilute sulphuric acid?

CHAPTER XVIII

SODIUM AND POTASSIUM COMPOUNDS

170. General Properties. — Sodium and potassium compounds may be studied together advantageously, as the corresponding compounds that the two elements form are very similar.

Most sodium and potassium compounds are white crystalline substances; practically all of them are soluble in water. With the exception of the hydroxides, all of those that we shall study are salts, possessing in a marked degree those properties which are characteristic of this class of bodies. As a rule, they are very stable compounds. They are among our most common and useful substances.

Sodium compounds are generally less soluble in water than are the corresponding potassium compounds; they are, therefore, not so satisfactory for certain uses. On the other hand, sodium salts are usually cheaper than those of potassium. Moreover, since the atomic weight of sodium is 23, while that of potassium is 39, a gram of a sodium salt contains a greater number of molecules than a gram of the corresponding potassium compound. Consequently a gram of a sodium salt will "go farther" than a gram of the corresponding potassium salt. For these reasons sodium compounds are generally used in manufacturing operations in preference to those of potassium.

PREPARATION OF THE HYDROXIDES

Of the methods in use for the manufacture of these hydroxides, two will be treated. In describing the oper-

ations, the sodium compound will be taken as a type for both.

171. Electrolytic Processes. — We saw (§ 74) that a water solution of sodium chloride, on being decomposed by an electric current, gives chlorine, hydrogen, and sodium hydroxide as products:

$$2\,NaCl + 2\,H_2O \longrightarrow 2\,NaOH + Cl_2 + H_2$$

The products of this reaction must not be allowed to mix during the electrolysis, lest other and more complicated changes take place.

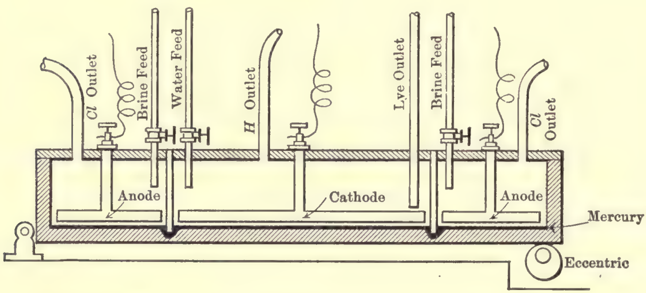
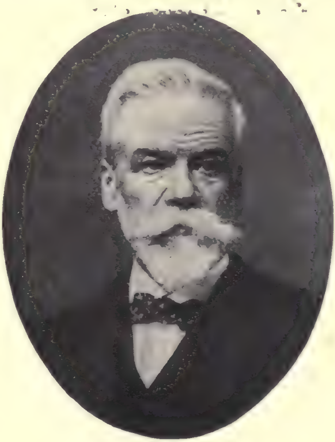


FIG. 41. — ELECTROLYTIC PREPARATION OF SODIUM HYDROXIDE.

(1) The Castner process is one of the earlier electrolytic methods that still ranks high for the production of pure sodium hydroxide. The apparatus (Fig. 41) consists of a stone cell, about 4 feet square and 6 inches deep, divided into three compartments. The end compartments contain a concentrated solution of salt. The middle compartment at first contains a dilute solution of sodium hydroxide. A layer of mercury covers the bottom of the cell, passing under the partitions, and keeps the solutions in adjacent compartments from mixing. The mercury is made to flow

Hamilton Young Castner (1857–1899) was born in Brooklyn, N.Y. His first success was in the reduction of the price of aluminum, then obtainable only by the use of sodium, from $10 to $1 per pound, by cheapening the production of sodium. But this process was destined to be superseded by Hall's still cheaper electrolytic method. Castner's most important invention is the electrolytic method by which we get pure sodium hydroxide directly from common salt.

Ernest Solvay was born in Belgium in 1839 and still lives in Brussels. He made practical a process for obtaining the carbonates of sodium directly from common salt by a precipitation method. His process is the only one used in this country. Solvay has received many honors and great wealth as a result of his discovery. He has been prominent in the political life of his country and has been a member of the Belgian Senate.



backward and forward by rocking the apparatus by means of an eccentric, which causes one end of the cell to be raised and then lowered half an inch. Carbon anodes are placed in the end compartments and an iron cathode in the middle compartment.

The current passes from the anode through the salt solution to the mercury, and then from the mercury through the sodium hydroxide solution to the iron cathode. This makes the mercury negative relative to the carbon anodes, and positive relative to the iron cathode. Chlorine ions pass to the anodes, where chlorine gas is liberated and drawn from the apparatus. The sodium ions pass to the mercury and the sodium is carried with the mercury to the middle compartment. Here sodium ions pass to the iron cathode, lose their electric charges, and at once react with the water. Sodium hydroxide and hydrogen result from the reaction.

In this way a solution containing about 27 % of sodium hydroxide is obtained. The solution is drawn off, the water evaporated, and the sodium hydroxide obtained pure as a white solid. This is melted and cast into sticks or run into iron drums. The chlorine which is obtained as a *by-product* is used to make bleaching powder. The hydrogen is not utilized.

(2) Large quantities of sodium hydroxide that is sufficiently pure for technical purposes are made by the electrolysis of solutions of sodium chloride in vessels arranged so that the anode chamber is separated from the cathode chamber by a porous partition or diaphragm. A concentrated solution of salt is fed to the compartment containing the anode and the solution of sodium hydroxide formed at the cathode is drawn off continually. The chlorine which is obtained as a *by-product* is either liquefied and shipped in that form for use, or is utilized for the manufacture of

chlorine compounds such as bleaching powder and carbon tetrachloride.

172. Lye Process. — Calcium hydroxide, $Ca(OH)_2$, ordinary slaked lime, is made from calcium oxide, CaO, unslaked lime, by adding water:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Calcium hydroxide is slightly soluble in water. If a solution of it is boiled with sodium carbonate, Na_2CO_3, the following reaction occurs:

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2\,NaOH + CaCO_3$$

The calcium carbonate, $CaCO_3$, formed is insoluble. It is this fact that makes the action go to an end. The solution of sodium hydroxide is separated from the precipitated calcium carbonate and evaporated to dryness.

173. Properties of the Hydroxides. — The hydroxides are very strong bases. As we have seen, they neutralize acids, forming salts and water. These bases have such a corrosive action on animal and vegetable matter that they are called *caustic* alkalies. Solutions of either sodium hydroxide or potassium hydroxide readily dissolve silk and wool. Dilute solutions of these alkalies have little effect on cotton, but warm concentrated solutions react with the cotton fiber. This action is the first step in the manufacture of mercerized cotton. Glass is attacked by these hydroxides; and although the action is somewhat slow, a solution of either hydroxide on standing in a glass bottle becomes quite impure. Both sodium and potassium hydroxides are very deliquescent substances.

174. Uses. — Sodium hydroxide, *caustic soda*, is manufactured in enormous quantities for use in soap making.

It is also used in making bleaching solutions, and in numerous other operations. Potassium hydroxide, *caustic potash*, is not so extensively used in manufacturing operations. It is used to make other compounds of potassium, and in the preparation of some soaps.

175. Sodium Peroxide. — This compound is made by heating slices of sodium in air freed from carbon dioxide:

$$2\,Na + O_2 \longrightarrow Na_2O_2$$

The temperature for the reaction must be kept between 300° C. and 400° C.

Sodium peroxide reacts violently with water, producing sodium hydroxide and oxygen:

$$2\,Na_2O_2 + 2\,H_2O \longrightarrow 4\,NaOH + O_2$$

When the reaction is carefully regulated, it is a most convenient laboratory method for making small quantities of oxygen. Sodium peroxide should never be left on paper or other combustible material, as the heat of reaction with moisture may cause a blaze. Sodium peroxide is useful for making solutions of hydrogen peroxide for laboratory use, by sifting the powder into very dilute acid solutions:

$$Na_2O_2 + 2\,HCl \longrightarrow H_2O_2 + 2\,NaCl$$

The use of sodium peroxide as an oxidizing and bleaching agent is increasing.

176. Sources of Sodium Chloride. — Sodium chloride, NaCl, *common salt*, is the most abundant sodium compound found in nature. Rock salt, or halite (Fig. 42), is found in many countries, but the largest deposits are those in New York, Louisiana, Austria, Germany, and Spain. Often in these beds the salt is of such purity that it has only to be mined and crushed to be ready for use.

Much of the salt in this country is obtained from salt wells in New York, Michigan, Ohio, and other states. Several borings are made and water sent down some of them (Fig. 43, *a*) to the salt bed. There brine is formed and forced, or pumped, through other borings (*b*) to the surface. The earthy impurities in the brine settle, and then it is evaporated, usually under reduced pressure. A fairly pure salt is thus obtained.

FIG. 42. — ROCK SALT.

The total amount of salt found in deposits, however, is insignificant compared with the quantity contained in the seas and oceans. The percentage of salt in sea water is small, yet it has been computed that the total quantity in the sea is 36,000,000,000,000,000 tons. The percentage of salt is

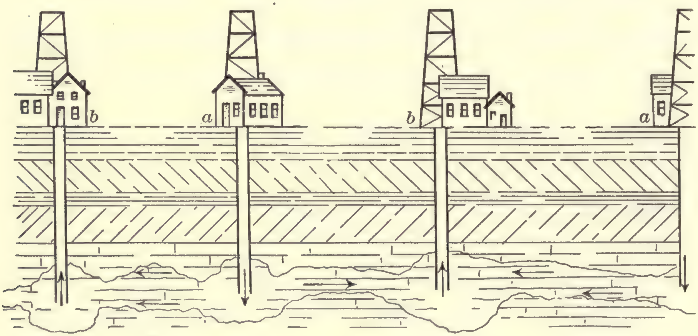


FIG. 43. — DIAGRAM OF SALT WELLS.

a, works at which water is pumped to salt strata; *b*, works at which brine is pumped to surface.

not uniform for all seas and oceans. These variations depend upon the ratio existing between the amount of water delivered by rivers to a sea and the amount lost by evapora-

FIG. 44. — COLLECTING SALT AFTER EVAPORATION IN RUSSIAN SALT FIELDS

tion. Thus, in the Baltic Sea, the inflow of river water, which contains much less salt than sea water, exceeds the loss by evaporation. Hence the water of the Baltic is relatively fresh. In the Dead Sea the reverse conditions

prevail; evaporation exceeds the inflow, and a solution approaching saturation has resulted. The average amounts of salts contained in one hundred parts of sea water are:

Dead Sea	22.0 parts	Atlantic Ocean	3.6 parts
Mediterranean	3.8 parts	Baltic	0.5 part

177. Extraction of Salt from Sea Water. — The method employed for getting salt from sea water depends upon the climate. In warm countries the sea water is evaporated by the sun's heat in shallow basins (Fig. 44). The salt that thus crystallizes is not very pure. In cold countries like northern Russia, sea water is allowed to freeze in flat basins. The coating of ice, which contains very little salt, is removed, and the process repeated till a concentrated brine is obtained, which it will pay to evaporate by artificial heat.

178. Purification of Salt. — Common salt contains several impurities. The principal impurity is magnesium chloride, a deliquescent substance which causes ordinary salt to cake. To get the pure sodium chloride, hydrogen chloride is passed into a saturated brine, or concentrated hydrochloric acid is added. Pure salt separates, because it is less soluble in a solution of hydrochloric acid than in water (§ 168).

179. Properties and Uses of Sodium Chloride. — Sodium chloride crystallizes in transparent cubes. Generally these cubes arrange themselves in four-sided, hollow pyramids, known as *hopper crystals* (Fig. 45). Water is often mechanically included in the crystals when salt separates from solution. When such crystals are heated, the inclosed water, being converted into steam, is violently expelled with a crackling noise and the flying about of small

particles of salt. This action is known as *decrepitation.* Sodium chloride is but slightly more soluble in hot water than in cold. It vaporizes slowly at a red heat.

Sodium chloride is typical of one of the three great classes of chemical compounds. It was the first representative of its class to become familiar to man. Other compounds with properties similar to common salt became known as *salts.* For a long time the term *salt* meant a white substance soluble in water, with a taste resembling common salt. Many compounds now known as salts possess neither of these properties. A water solution of a salt, like sodium chloride, does not change the color of litmus. Like most salts, sodium chloride is composed of a metallic element and a nonmetallic constitutent.

Salt is indispensable as a food for the higher animals. It furnishes the chlorine needed for the hydrochloric acid in the gastric juice. Tons of common salt are used every year in the preparation of sodium carbonate and sodium hydroxide. Enormous quantities of salt are consumed in refrigeration and in curing meat and fish.

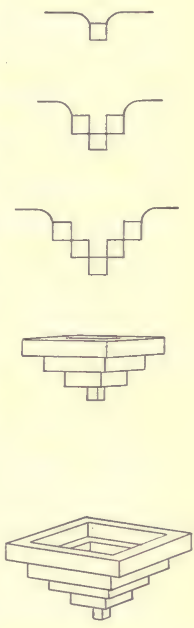


FIG. 45.

180. Potassium Chloride. — The chloride of potassium, KCl, is also found in sea water, but in smaller quantities than sodium chloride. Its most important source is the mineral deposits at Stassfurt, Germany.

The properties of potassium chloride are similar to those of sodium chloride, but the potassium compound is more

soluble in water. The chloride is used in the manufacture of other potassium compounds, particularly the nitrate and the chlorate.

Potassium chloride is extensively used in the manufacture of fertilizers, because it is the cheapest compound of potassium, an element essential to plant life.

181. Occurrence and Preparation of the Carbonates (Na_2CO_3, K_2CO_3). — These important compounds occur only to a very limited extent in nature. The ashes of land plants contain potassium carbonate, and the ashes of sea plants both sodium and potassium carbonates.

The most important process for the manufacture of sodium carbonate and sodium bicarbonate is the *Solvay process*.

The gas ammonia, NH_3, is the anhydride (§ 210) of the base ammonium hydroxide, NH_4OH; in other words, it will unite with water to form ammonium hydroxide:

(1) $$NH_3 + H_2O \longrightarrow NH_4OH$$

Carbon dioxide (carbonic anhydride) unites with water to form an acid, carbonic acid, H_2CO_3:

(2) $$CO_2 + H_2O \longrightarrow H_2CO_3$$

When ammonium hydroxide is brought in contact with an excess of carbonic acid, all of the OH^- ions of the base unite with H^+ ions from the acid and the solution will contain ammonium hydrogen carbonate or ammonium bicarbonate:

(3) $$NH_4OH + H_2CO_3 \longrightarrow H_2O + NH_4HCO_3$$

If a solution of ammonium bicarbonate comes in contact with a solution of sodium chloride, sodium bicarbonate

will separate, because it is insoluble under the conditions of the experiment:

$$(4) \qquad NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$

The above considerations may aid in obtaining equation (5), generally written to represent the Solvay process. Equation (5) is the sum of equations (1), (2), (3), and (4).

$$(5) \quad NaCl + H_2O + CO_2 + NH_3 \longrightarrow NaHCO_3 + NH_4Cl$$

In practice the operation is carried out by saturating a concentrated brine with ammonia and then passing carbon dioxide into this mixture under pressure.

The sodium bicarbonate is separated by filtration and purified. The impure sodium bicarbonate remaining after the filtration of the liquid is washed with water, dried, and then heated to drive off volatile impurities and to convert it into pure sodium carbonate:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

The pure sodium carbonate thus obtained may be (*a*) placed on the market as anhydrous sodium carbonate (soda ash); (*b*) crystallized from water solution and sold as washing soda, $Na_2CO_3 \cdot 10\ H_2O$; (*c*) reconverted into pure sodium bicarbonate, baking soda, $NaHCO_3$:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\ NaHCO_3$$

It is a matter of great importance to produce sodium carbonate at low cost. For this reason the above reactions are carried out so that the by-products are utilized. The ammonium chloride is used to furnish ammonia to saturate a fresh supply of brine. The carbon dioxide that is given off in decomposing sodium bicarbonate furnishes part of the supply of that gas needed in the first step of the operation.

182. Uses of the Carbonates. — Two uses of the carbonates of sodium have been implied in the names washing soda and baking soda. The former has, in a modified way, the properties of sodium hydroxide. It is often called "soda." In the refining of petroleum, sodium carbonate is used to neutralize sulphuric acid. It dissolves many substances, especially oils or fats, and hence it is an excellent cleansing substance. It is usually an important constituent of cleaning powders. Both washing soda and baking soda liberate carbon dioxide when treated with acids:

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

Taking into consideration the molecular weights, we see from these equations that for equal weights of the carbonates, baking soda furnishes the greater amount of carbon dioxide. It is consequently preferred for those uses, as in baking powder, in which the liberation of carbon dioxide is required.

Sodium bicarbonate is used in chemical fire extinguishers, is an important constituent of baking powders, and is used in the manufacture of effervescent salts.

183. Hydrolysis. — Water solutions of sodium carbonate and of sodium bicarbonate are not neutral, but alkaline. This depends upon the slight dissociation of water, a condition which was not taken into account in the discussion of the dissociation of compounds:

$$H_2O \rightleftarrows H^+ + OH^-$$

In most cases the few hydrogen and hydroxyl ions from the dissociation of the solvent have little effect, but their presence must be reckoned with when the solution contains a compound which is but slightly more dissociated

than water itself, *e.g.* carbonic acid, H_2CO_3. When sodium carbonate, one of the salts of this acid, dissolves, it largely dissociates into Na^+ ions and CO_3^{--} ions. All of the hydrogen ions from the water, however, cannot remain as such in the presence of CO_3^{--} ions, because undissociated carbonic acid will be formed:

$$2\,(H^+) + CO_3^{--} \longrightarrow H_2CO_3$$

The withdrawal of the hydrogen ions to form an undissociated compound disturbs the equilibrium of water with its ions, and a few molecules of water will have to dissociate in order to restore it. Most of the newly formed hydrogen ions likewise pass into the undissociated carbonic acid. This process of dissociation and combination is repeated till an equilibrium is established. It must be remembered, however, that the progressive dissociation of water gave OH^- ions as well as H^+ ions. These hydroxyl ions have little tendency to combine with the Na^+ ions to form undissociated sodium hydroxide, but simply remain in solution as ions of this strongly dissociated compound. There are enough of these hydroxyl ions to give the blue reaction with litmus.

All these changes may be expressed by the equation:

$$2\,(Na^+) + CO_3^{--} + 2\,(H^+) + 2\,(OH^-) \longrightarrow H_2CO_3 + 2\,(Na^+) + 2\,(OH^-)$$

Such a change, involving water, is known as *hydrolysis*, and is the reverse of neutralization. Carbonic acid, being but slightly dissociated in water solution, is a weak acid, while sodium hydroxide is a strongly dissociated base. Hence sodium carbonate is a *salt formed by a weak acid with a strong base*. Such salts undergo hydrolysis when dissolved in water, and their solutions give *alkaline* reactions. Sodium acetate, sodium cyanide, and sodium sulphide are salts of this character.

Some salts, as copper sulphate, give an *acid* reaction in water solution. This is also a case of hydrolysis:

$$Cu^{++} + SO_4^{--} + 2(H^+) + 2(OH^-) \longrightarrow Cu(OH)_2 + 2(H^+) + SO_4^{--}$$

A detailed explanation would show that nearly all the OH^{--} ions from the dissociation of the water combine with the Cu^{++} ions to form undissociated copper hydroxide, a very *weak* base. The hydrogen ions from the water are present at the end of the hydrolysis as ions of the strongly dissociated sulphuric acid. These hydrogen ions give the red effect with litmus, and the acid reaction of a solution of copper sulphate is accounted for.

The acid reaction of solutions of such salts, *formed by a weak base with a strong acid*, is due to hydrolysis. Zinc sulphate, aluminum sulphate, and ferric chloride are salts of this kind.

Salts formed by strong acids with strong bases are not subject to hydrolysis, since their ions have little tendency to combine with the H^+ and OH^- ions of water to form undissociated compounds. The solutions of such salts are neutral. Sodium chloride and potassium nitrate belong to this class.

In general, hydrolysis is possible with a salt only when either the acid or base forming it, or both, are weak.

184. Occurrence of the Nitrates ($NaNO_3$, KNO_3). — Both sodium and potassium nitrates occur in small quantities in the soil. They are formed by nitrogenous organic matter decaying in contact with soluble sodium or potassium compounds.

Deposits of sodium nitrate, covering an area of over four hundred square miles, are found in desert regions along the western coast of South America. These beds lie near

the boundary lines of Peru, Chile, and Bolivia and have been the cause of many disputes between these countries. The boundary lines have now been so adjusted that Chile owns the greater portion of these extremely valuable deposits. The crude nitrate is obtained by crushing the loose, rocky material of the beds and boiling it in water. The liquor containing the nitrate is run off and allowed to crystallize. The product, crude Chile saltpeter, contains 94 % to 98 % of sodium nitrate. A purer quality is obtained by recrystallization.

185. Manufacture of Potassium Nitrate. — Most of the potassium nitrate (niter) now used is prepared from sodium nitrate. The potassium compound is made by mixing hot, concentrated solutions of sodium nitrate and potassium chloride. The equation for the reaction is:

$$KCl + NaNO_3 \longrightarrow KNO_3 + NaCl$$

On evaporation the boiling mixture first deposits common salt, since this substance is less soluble in boiling water than is potassium nitrate. On cooling the solution, however, the potassium nitrate crystallizes out, because it is far less soluble in cold than in hot water. A purer quality of potassium nitrate can be obtained by recrystallization.

186. Properties of the Nitrates. — Sodium and potassium nitrates are white, soluble salts. Sodium nitrate differs from the potassium compound in crystalline form and in being hygroscopic. Both nitrates give off oxygen when heated, and leave compounds, known as nitrites, containing less oxygen.

187. Uses. — The principal use of potassium nitrate (ordinary saltpeter) is in the manufacture of black gunpowder. Potassium nitrate is also used to preserve meat,

and corned beef owes its red color to this treatment. The cheaper sodium nitrate has replaced potassium nitrate in the manufacture of nitric acid and its derivatives. Chile saltpeter is also used as a fertilizer, and in the manufacture of sodium nitrite, a most important substance in the manufacture of aniline dyes.

188. Sodium Nitrite is a by-product obtained in the manufacture of a fine quality of red lead by the addition of molten lead to sodium nitrate:

$$3\,Pb + 4\,NaNO_3 \longrightarrow Pb_3O_4 + 4\,NaNO_2$$

SUMMARY

The **hydroxides** of sodium and potassium are prepared by the electrolysis of solutions of the chlorides, and by the reaction of the carbonates with slaked lime.

Sodium **peroxide** is made by burning sodium in air. It is used as an oxidizing agent.

The **chlorides** of these two metals occur in nature.

They are typical salts. They have a saline taste, are neutral, and result from the action of the corresponding acid and base.

The chlorides are used in the preparation of other sodium and potassium compounds.

The **carbonates** occur in plant ashes.

They are commercially prepared by the decomposition of the bicarbonates by heat.

The carbonates are used in the preparation of soaps, washing powders, glass, and in making other compounds.

The **bicarbonates** are made commercially by the action of carbon dioxide with ammoniacal solutions of the chlorides.

They are only slightly soluble and are less corrosive than the carbonates.

Sodium bicarbonate is a constituent of all baking powders and is used in chemical fire extinguishers.

Sodium **nitrate** is obtained from Chile. Potassium nitrate is formed by the reaction of potassium chloride with sodium nitrate.

Sodium nitrate is used to prepare potassium nitrate, also as a fertilizer and as a source of nitric acid. Potassium nitrate is used in gunpowder.

EXERCISES

1. How could you show that there are potassium compounds in plants?

2. Describe one process used for the preparation of sodium hydroxide.

3. Compare the properties of sodium hydroxide with those of potassium hydroxide.

4. What oxide is made by burning sodium in air? What is this oxide used for?

5. How many liters of oxygen could be obtained from 30 grams of sodium peroxide by its reaction with water?

6. Cite cases to show that salt is of great importance to chemical industries.

7. Mention three ways in which salt is obtained.

8. Why does table salt "cake"?

9. How could pure sodium chloride be obtained from salt?

10. Why was sodium carbonate obtained from the ashes of sea plants and not from the water directly?

11. Write the equations for the preparation of sodium carbonate by the Solvay process.

12. In getting the normal carbonate, in the Solvay process, why do we have to get the bicarbonate first and then decompose it?

13. What advantage has baking soda over potassium bicarbonate?

14. Equal weights being taken, which will neutralize the larger quantity of acid, sodium hydroxide or potassium hydroxide? Sodium carbonate or bicarbonate?

15. Why is "soda" used in cleaning?

16. What objection is there to using solutions of washing soda to cleanse woolen goods?

17. How could you distinguish chemically between washing soda and baking soda?

18. Would a water solution of sodium bicarbonate give an alkaline or an acid reaction? Explain.

19. How could you tell potassium nitrate from sodium nitrate?

20. How are the nitrates produced in nature?

21. Why can potassium nitrate be obtained by a reaction between potassium chloride and sodium nitrate?

22. How many pounds of sodium nitrite could be obtained from 200 pounds of sodium nitrate?

CHAPTER XIX

SULPHUR AND SULPHIDES

SULPHUR

189. Occurrence. — Sulphur is found in nature either free or in combination with other elements. In the uncombined or *native* state it is found in volcanic regions. The most extensive deposits of native sulphur are the Louisiana and Texas beds, where the sulphur is found 500 feet below the surface.

Sulphur is found combined with many different metals, as *sulphides;* those of iron, copper, lead, and zinc are the more abundant. The *sulphates* of a few metals are found in considerable quantities.

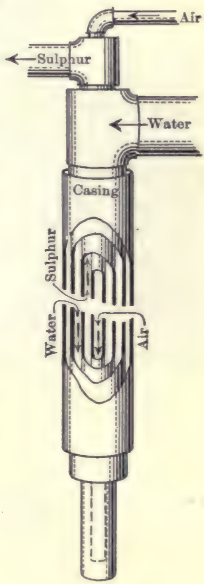


FIG. 46.

190. Extraction, Frasch Method. — On account of the overlying beds of quicksands, several companies failed to extract profitably the sulphur from the Louisiana deposits. It remained for Herman Frasch, an American chemist, to devise a most ingenious and scientific method.

In the Frasch process, a hole is drilled and piped down through the 500 feet of overlying deposits to the bottom of the sulphur bed, which is often 200 feet more. Inside the large pipe casing of the hole for the entire distance is

a 6-inch pipe, and inside this a 3-inch pipe, which in turn surrounds a 1-inch pipe (Fig. 46). Through the 6-inch pipe, water heated to 167° C. under a pressure of 100 pounds is forced down the well to melt the sulphur below. Hot, compressed air, coming down through the 1-inch pipe, mingles with the liquid sulphur and reduces the specific gravity of the liquid, so that it can be raised to the surface.

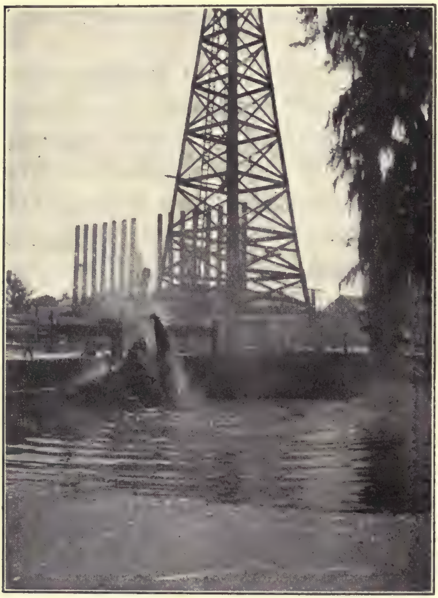


Fig. 47. — Stream of Sulphur Discharging into Bin.

The combined pressure of the column of hot water and the compressed air pumped in, raises the sulphur above the surface through the 3-inch pipe. Strainers at the bottom prevent earthy material from being driven upward. On reaching the surface, the melted sulphur is run into huge bins 60 feet high, made of rough boards (Fig. 47). The sulphur soon cools, forming an enormous block of solid sulphur of remarkable purity (99%). Some of the blocks contain 100,000 tons. The block is broken up by blasting (Fig. 48) and loaded on cars by steam shovels. The hole at the right of the center of the picture shows where liquid sulphur ran out when the surrounding solid mass was

Herman Frasch (1852–1914), a native of Würtemberg, took up the practice of pharmacy at sixteen. We find him, a few years after coming to America, establishing an industrial laboratory of his own. He secured patents on a wide variety of industrial processes, the most valuable relating to the refining of petroleum and to sulphur. His desulphurization of the Ohio and Canadian petroleums made these low-grade oils valuable. Where many had failed, he, after ten years of labor, developed a profitable method for extracting the Louisiana sulphur. He was awarded the Perkin Medal in 1912.

blasted away. This sulphur not only supplies the American market, but is shipped to Europe as well.

FIG. 48. — REMOVAL OF SULPHUR FROM BIN AFTER BLASTING.

191. Extraction, Sicilian Method. — The rocky material containing the sulphur produced in volcanoes is heaped into piles which are then covered with spent ore. Sufficient air is admitted to the pile to burn a small portion of the sulphur. The sulphur that burns produces sufficient heat to melt the remainder of the sulphur, which sinks down through the pile and runs out of the bottom into a collecting pool.

192. Purification. — This crude sulphur is purified by heating in iron retorts (Fig. 49) and passing the vaporized sulphur into brick chambers, where it deposits on the cool wall as a fine powder, known as *flowers of sulphur.*

Soon, however, the walls become warm and most of the vaporized sulphur condenses as a liquid, which makes its way to the outlet of the condensing chamber. It is then cast in wooden cylindrical molds about an inch and a half in diameter. This form is *roll sulphur*, or brimstone.

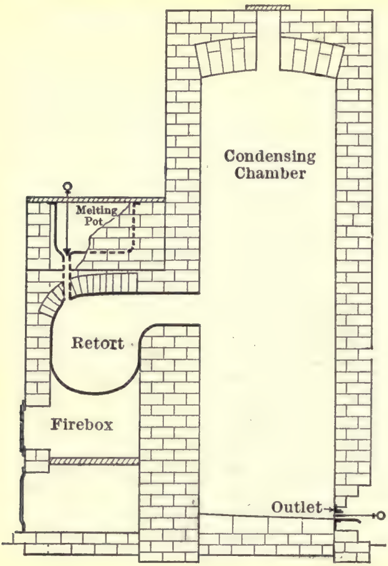


FIG. 49.—PURIFICATION OF SULPHUR.

193. Forms of Sulphur.—No element displays a greater variety of forms than sulphur. Three of these are well known and are easily obtained by the following methods:

(1) Crystallization from carbon disulphide.

Carbon disulphide dissolves powdered roll sulphur very readily. The solvent evaporates quickly at ordinary temperatures; so that as the solution stands, the sulphur soon begins to be deposited, just as salt is deposited when a solution of it is evaporated. The sulphur is deposited in crystals of a beautifully regular octahedral shape. This form is *orthorhombic* sulphur (Fig. 50). It is soluble in carbon disulphide, and has a density of 2.01.

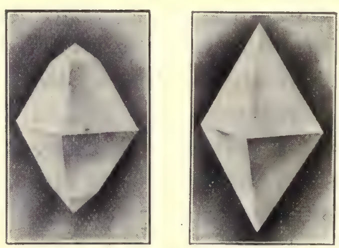


FIG. 50.—RHOMBIC SULPHUR CRYSTALS, MAGNIFIED.

(2) Crystallization of melted sulphur.

Sulphur is melted and then allowed to cool until crystals appear at the surface; on pouring off the still liquid sulphur, the solid part is found in crystals shaped like long, narrow prisms with sharp ends (Fig. 51). This kind of sulphur is known as *prismatic* sulphur. Its density is 1.96, and it differs in other properties from the rhombic variety (page 201). The prismatic form is unstable. On standing a few days, its crystals lose their transparency, become more brittle, and increase in density. Examination by *polarized light* shows that the long, narrow prisms have broken up into minute rhombic crystals.

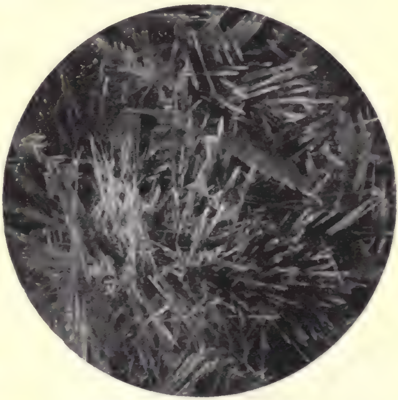


FIG. 51. — PRISMATIC SULPHUR.

(3) Sudden cooling of boiling sulphur.

By application of considerable heat sulphur can be made to boil. Before it reaches its boiling point (445°) it goes through some interesting and unusual changes. When just above its melting point, sulphur is a mobile liquid of a light amber color. As the temperature rises, the sulphur darkens rapidly and thickens so that it can hardly be poured from the inverted test tube; on further heating, it again becomes less viscous, and finally boils, forming a pale orange vapor.

When boiling sulphur is poured into cold water, the cooled sulphur assumes a form (Fig. 52) quite different in appearance from any of those forms already described. It is without crystalline form, of a rubber-like consistency,

and light amber in color. Because of its lack of crystalline form it is called *amorphous* sulphur. This differs from the rhombic form in being insoluble in carbon disulphide. It is sometimes spoken of as *plastic sulphur.* Like prismatic sulphur, it is unstable and is changed in the course of a few days into the stable rhombic form. In this change the amorphous sulphur loses its plastic character and becomes soluble in carbon disulphide.


FIG. 52. — AMORPHOUS SULPHUR.

If sulphur is dissolved in some alkali, as sodium hydroxide, and hydrochloric acid added to the solution, a white, finely divided precipitate is obtained. This precipitate is a form of amorphous sulphur. When shaken with water it gives a fluid known as *milk of sulphur.*

194. Allotropic Forms. — A number of other elements besides sulphur occur in several different modifications, known as allotropic forms. The graphite used in lead pencils and the diamond are two of the allotropic forms of carbon. These two forms are strikingly different in physical properties, but they are the same element, carbon. Oxygen and ozone are allotropic forms. *Allotropic forms are varieties of the same element, differing in properties on account of varying energy content.* They can be converted into one another.

195. Stability of the Allotropic Forms. — At temperatures up to 96° C. all forms of sulphur tend to assume the rhom-

bic form. From 96° to 114° the stable form is the prismatic variety. If crystals of the rhombic variety are put into a test tube and kept standing in boiling water for several days, the form will be changed to minute crystals of the prismatic variety. Thus it is seen that the form which the sulphur assumes depends on the temperature. It is generally true that each of the allotropic forms of any element is stable under certain definite conditions.

Roll sulphur consists entirely of the rhombic variety. Flowers of sulphur are made up of the rhombic form together with a smaller proportion of the amorphous form, as is shown by the fact that flowers of sulphur are only partly soluble in carbon disulphide.

196. Chemical Properties. — All forms of sulphur burn readily when heated in the presence of oxygen; sulphur dioxide is formed as a product of the action. Sulphur is capable of taking oxygen away from compounds:

$$S + O_2 \longrightarrow SO_2$$

It does not, however, make a very satisfactory reducing agent, because it is apt to combine with the products of the reduction.

FIG. 53.

Sulphur is a moderately active element. It combines readily with many metals, often with the evolution of light and heat. In a sense, then, it may be said to support combustion. This can be shown by heating sulphur in a test tube until it boils and the sulphur vapor nearly fills the tube; on placing a strip of very

thin copper in the tube, it takes fire and burns, copper sulphide being formed:

$$Cu + S \longrightarrow CuS$$

Powdered zinc and sulphur, if mixed in certain proportions, will combine almost explosively when ignited, with the formation of zinc sulphide (Fig. 53):

$$Zn + S \longrightarrow ZnS$$

Sulphur does not unite very readily with non-metals. Such compounds are, in general, not very stable.

197. Sulphides. — The metallic sulphides form a very important class of compounds. Many metals are extracted from sulphide ores. Most of the sulphides, excepting those of the extremely metallic elements, are insoluble in water. They usually have characteristic colors.

The blackening or tarnishing of metals is sometimes due to the action of sulphur. This is particularly true of silver. Sulphur or sulphur compounds get into the air from illuminating gas or burning coal and, acting on silver, produces the black sulphide.

The tarnishing of silverware by the yolk of an egg or by mustard is due to the sulphur compounds contained in these substances. Brass and copper are also readily tarnished by sulphur and some of its compounds.

198. Resemblances of Sulphur to Other Elements. — In the ease with which it combines with other elements, particularly metals, sulphur resembles both chlorine and oxygen. Generally it displays the closer resemblance to oxygen. This is shown by comparing the solubility in water of oxides and sulphides. Those metals which form insoluble oxides also, as a rule, form insoluble sulphides.

In many of its compounds sulphur, like oxygen, has a valence of *two*. Therefore the sulphides and the oxides of many of the elements have similar formulas:

Element	Sulphide	Oxide
Copper	CuS	CuO
Zinc	ZnS	ZnO
Hydrogen	H_2S	H_2O
Magnesium	MgS	MgO
Mercury	HgS	HgO

199. Uses of Sulphur. — Sulphur is used in making sulphur dioxide, which is employed for bleaching and disinfecting. Sulphur or some compound of sulphur serves for the hardening (vulcanizing) of rubber. Sulphur is more or less important for the manufacture of fireworks and gunpowder, while increasing uses are in the making of carbon disulphide and the dyes known as sulphur colors. Sulphur is extensively used as a constituent of sprays used on trees.

HYDROGEN SULPHIDE

200. Preparation. — Hydrogen sulphide, H_2S, is formed slowly and in small quantity when hydrogen is passed over heated sulphur (Fig. 54). The presence of the gas is shown by the blackening of a strip of paper (*aa*) moistened with lead acetate. The difficulty of forming hydrogen sulphide by the direct union of the elements is in strong contrast to the great readiness with which the hydrogen compounds, so far studied, are formed. The lack of a strong tendency

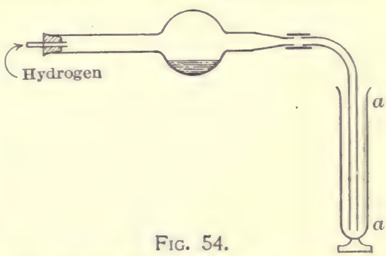


Fig. 54.

of hydrogen and sulphur to combine indicates the unstable character of their product.

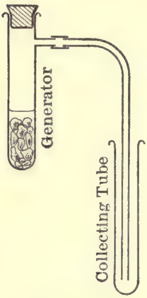


FIG. 55.

When albumen or other organic matter, containing sulphur, decays, hydrogen sulphide is one of the substances formed. If a little sulphur is added to a fermenting sugar solution, hydrogen sulphide is produced.

For practical use hydrogen sulphide is readily formed by the action of dilute hydrochloric acid on ferrous sulphide (Fig. 55):

$$FeS + 2\,HCl \longrightarrow FeCl_2 + H_2S$$

The hydrogen sulphide passes off readily as a gas; for this reason the double decomposition proceeds rapidly. The sulphides of some other metals could be used in place of the ferrous sulphide, and instead of hydrochloric acid dilute sulphuric acid might be used. The gas may be collected by downward displacement.

201. Physical Properties. — Hydrogen sulphide is a colorless gas, slightly heavier than air, having a characteristic odor resembling rotten eggs. It dissolves to some extent in water, and therefore is not usually collected over this liquid. It is generally collected by the displacement of air. A water solution of the gas is sometimes used in the laboratory, but in such a solution the gas is decomposed in a few days by action with the oxygen of the air. Besides being unpleasant, it is injurious to inhale the gas, as headache and sickness are apt to result.

202. Chemical Properties. — The gas burns readily, if there is an ample supply of oxygen, forming water and

sulphur dioxide; with a limited quantity of oxygen, sulphur is formed:

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$
$$2\,H_2S + O_2 \longrightarrow 2\,H_2O + 2\,S$$

On being heated moderately, hydrogen sulphide breaks up into hydrogen and sulphur.

The fact that a water solution of hydrogen sulphide is a poor conductor of electricity, shows that as an acid it is very weak. The solution reddens blue litmus very slowly, and the color is never as deep as that produced by solutions of strong acids.

203. Formation of Sulphides. — Hydrogen sulphide acts on most metals, forming sulphides and liberating hydrogen:

$$Pb + H_2S \longrightarrow PbS + H_2$$
$$2\,Ag + H_2S \longrightarrow Ag_2S + H_2$$

If hydrogen sulphide is passed into a solution of copper sulphate, copper sulphide is formed:

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4$$

A similar reaction occurs with the dissolved salts of many metals, as lead, silver, and tin. In such cases the determining factor that makes the action possible is the insolubility of the metallic sulphide either in water or in the dilute acid that is formed as a result of the action. We have seen that metallic sulphides can generally be formed in three different ways, for example:

$$2\,Ag + S \longrightarrow Ag_2S$$
$$2\,Ag + H_2S \longrightarrow Ag_2S + H_2$$
$$2\,AgNO_3 + H_2S \longrightarrow Ag_2S + 2\,HNO_3$$

The possibility of precipitating metallic sulphides by this third method is of great value to the analytical chemist

in determining the composition of unknown substances. The identification of the metal in a particular case is made by means of the color of the sulphide, its solubility in various reagents, or other characteristic reactions.

TABLE OF SULPHIDES

NAME	FORMULA	COLOR	DISSOLVES IN
Mercuric sulphide	HgS	Black	Aqua regia
Copper sulphide	CuS	Black	Concentrated nitric acid
Cadmium sulphide	CdS	Yellow	Concentrated nitric acid
Arsenic sulphide	As_2S_3	Yellow	Yellow ammonium sulphide
Antimony sulphide	Sb_2S_3	Orange	Yellow ammonium sulphide
Zinc sulphide	ZnS	White	Dilute acids

204. Sulphur Springs. — Hydrogen sulphide is produced in nature in several ways. We have mentioned its production during the decay of certain organic matter. Calcium sulphide is formed when decaying matter reduces calcium sulphate. Water reacts with calcium sulphide, forming calcium hydroxide and hydrogen sulphide; the calcium hydroxide is converted into the carbonate by the action of water containing carbon dioxide.

$$CaSO_4 - 4\,O \longrightarrow CaS$$
$$CaS + 2\,H_2O \longrightarrow H_2S + Ca(OH)_2$$
$$Ca(OH)_2 + H_2CO_3 \longrightarrow CaCO_3 + 2\,H_2O$$

The presence of hydrogen sulphide in the waters of some sulphur springs is accounted for by these reactions.

SUMMARY

Sulphur is found uncombined (native), or combined in the form of sulphides and sulphates. In Louisiana it is melted underground

and forced to the surface. It is extracted in Sicily by melting it out from the earth with which it is mixed.

Commercial forms of sulphur are flowers of sulphur and lump sulphur.

Allotropic forms of an element are varieties of the same element differing in properties.

Allotropic forms of sulphur are the rhombic, the prismatic, and the amorphous. The latter exists in several modifications.

	Rhombic Sulphur	Prismatic Sulphur
Specific gravity	2.07	1.96
Solubility	Soluble in carbon disulphide	Insoluble in carbon disulphide
Stability	Stable below 96°	Stable between 96° and 114°

Sulphur **melts** at 114° and **boils** at 445°; it is a non-conductor of electricity.

Sulphur is a **moderately active** element, burns in air, and unites directly with many elements.

Sulphur is used for making sulphur dioxide, sulphur acids, sulphides, and carbon disulphide. Rubber is vulcanized by sulphur or some of its compounds.

Hydrogen sulphide occurs in volcanic gases and in water of sulphur springs, and is formed in nature by decay of organic matter containing sulphur.

Hydrogen sulphide is prepared by the action of hydrochloric acid or of sulphuric acid with ferrous sulphide.

It is a colorless gas, poisonous, and possessing a characteristic, disgusting odor. One volume of water at 20° dissolves 3.1 volumes of hydrogen sulphide.

The water solution is a weak acid and forms sulphides with most metallic ions.

The gas burns in a limited supply of air to form water and sulphur, and in an excess of air forms water and sulphur dioxide.

Hydrogen sulphide is used by chemists to precipitate certain metals from solutions as sulphides.

EXERCISES

1. Compare, as to efficiency, the Sicilian with the Louisiana process for the extraction of sulphur.

2. Describe the process that a piece of native sulphur undergoes before it is placed on the market as flowers of sulphur.

3. Explain (in the Louisana process for obtaining sulphur) the uses of (*a*) the hot water, (*b*) the hot, compressed air, (*c*) the wooden bins.

4. What is meant by the *allotropic forms* of an element? Name the allotropic forms of sulphur.

5. State what allotropic forms of sulphur exist in each of the following commercial varieties: roll sulphur, milk of sulphur, and flowers of sulphur.

6. What conditions determine whether sulphur is to assume the prismatic or the rhombic form?

7. How would you prepare milk of sulphur from a piece of roll sulphur?

8. Why is a sulphur candle sometimes used for fumigation?

9. Why does silverware tarnish so readily in large cities?

10. Write the formulas of five sulphides and the formulas of the corresponding oxides.

11. Starting with iron, sulphur, and hydrochloric acid, give directions for the preparation of hydrogen sulphide.

12. How many grams of ferrous sulphide would be required for the preparation of five liters of hydrogen sulphide?

13. Account for the particles of sulphur found in a bottle in which a water solution of hydrogen sulphide has been standing for some days. How would the contents smell? Write the equation for the reaction that has taken place.

14. Under what conditions is sulphur deposited when hydrogen sulphide burns?

15. How many liters of oxygen would be required for the complete combustion of four liters of hydrogen sulphide?

16. Account for the fact that a water solution of hydrogen sulphide is not so active an acid as a water solution of hydrogen chloride.

17. How many grams of hydrogen sulphide would be required to combine with the copper in 0.1 gram of copper sulphate?

18. Account for the unpleasant taste of the waters of sulphur springs.

19. Calculate the weight of a liter of hydrogen sulphide measured under standard conditions.

20. How could hydrogen sulphide be used to distinguish the solution of a zinc salt from a solution of a copper salt?

H_2O

H_2O

$2Fe + S + 2HCl \rightarrow H_2S + 2FeCl_2$

CHAPTER XX

OXIDES AND ACIDS OF SULPHUR

SULPHUR DIOXIDE

205. Preparation by Direct Combination. — When sulphur burns in oxygen or in air, sulphur dioxide is formed:

$$S + O_2 \longrightarrow SO_2$$

The odor of burning sulphur is due to the dioxide formed. Many ores are sulphides of metals, and large quantities of sulphur dioxide are prepared by roasting such ores in air.

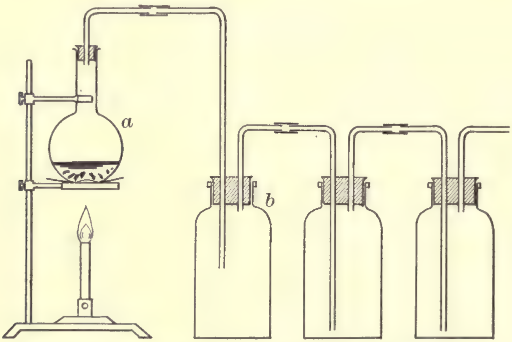


FIG. 56. — PREPARATION OF SULPHUR DIOXIDE.
a, generator; *b*, safety bottle.

206. Preparation by Reduction of Sulphuric Acid. — When copper, silver, or mercury is treated with hot, concentrated sulphuric acid, sulphur dioxide is formed (Fig. 56). The chemical action is complicated, but it is probable that

the acid first acts with the metal, and hydrogen is displaced, according to the equation:

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + 2\,H$$

The hydrogen is then oxidized to water by the excess of hot, concentrated sulphuric acid. This oxidation is accomplished at the expense of the reduction of the sulphuric acid to sulphurous acid, according to the equation:

$$H_2SO_4 + 2\,H \longrightarrow H_2SO_3 + H_2O$$

The sulphurous acid decomposes, as soon as it is formed, into water and sulphur dioxide, according to the equation:

$$H_2SO_3 \longrightarrow H_2O + SO_2$$

The changes indicated in the three equations given above go on together. The total change may be represented by the one equation:

$$Cu + 2\,H_2SO_4 \longrightarrow CuSO_4 + 2\,H_2O + SO_2$$

Some copper sulphide is formed by the reaction of copper with hot, concentrated sulphuric acid.

207. Preparation by Decomposition of a Sulphite. — When a mixture of sodium sulphite and dilute sulphuric acid is gently heated in a flask, sulphur dioxide is evolved, according to the equation:

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$

Possibly sulphurous acid is first formed, but if so, this unstable compound immediately decomposes into water and sulphur dioxide. The equations are:

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2SO_3$$
$$H_2SO_3 \longrightarrow H_2O + SO_2$$

The evolution of the gas may be made very regular by using sodium acid sulphite and allowing sulphuric acid (1 to 1) to fall on it, drop by drop (Fig. 57).

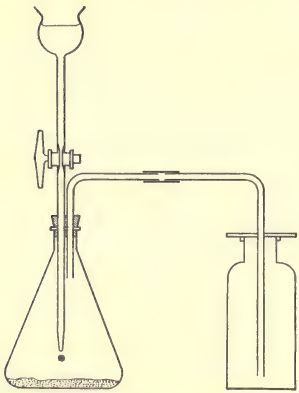


FIG. 57.

208. Physical Properties. — Pure sulphur dioxide is a colorless gas, with a suffocating odor, and is more than twice as heavy as air. It is very soluble in water; one volume of water dissolves many times its own volume of the gas at ordinary temperatures. The gas may be completely expelled from the solution by boiling.

Sulphur dioxide is one of the easiest gases to liquefy. At ordinary temperatures, a pressure of but two atmospheres is required; at the temperature of a freezing mixture of ice and salt, the ordinary atmospheric pressure is sufficient to change the gas to a liquid. Liquid sulphur dioxide is sold in glass or metal siphons (Fig. 58).

FIG. 58.

209. Chemical Properties. — The solution of sulphur dioxide has an acid reaction and neutralizes bases, forming sulphites. Thus with sodium hy-

droxide the reaction results in the formation of sodium sulphite and water. This indicates the presence in the solution of hydrogen and sulphite ions, or, in other words, the solution contains sulphurous acid. This acid, however, has never been separated from the solution. The acid is formed according to the equation :

$$H_2O + SO_2 \longrightarrow H_2SO_3$$

If a solution of sulphurous acid is allowed to stand in contact with air, it gradually takes up oxygen, forming sulphuric acid, according to the equation :

$$2\,H_2SO_3 + O_2 \longrightarrow 2\,H_2SO_4$$

Sulphites are likewise changed to sulphates.

210. Anhydrides. — Many oxides unite with one or more molecules of water to form new compounds. Such oxides are called *anhydrides* (meaning "without water"). An anhydride is an oxide which unites with water to form an acid or a base. Anhydrides are classified as *acid* or *basic*, according to whether they form acids or bases in combining with water. Calcium oxide, CaO, is a basic anhydride, as shown by the equation :

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Slaked lime, $Ca(OH)_2$, is a base. Since sulphur dioxide unites with water to form an acid, it is called an *acid anhydride.* An acid anhydride is named from the acid it forms when it unites with water. Hence sulphur dioxide is called sulphurous anhydride.

211. Reducing Action of Sulphur Dioxide. — Since sulphurous acid is so readily oxidized, it acts as a reducing agent in many cases. Potassium permanganate is reduced by

sulphurous acid to potassium sulphate and manganese sulphate:

$$2\,KMnO_4 + 5\,H_2SO_3 \longrightarrow K_2SO_4 + 2\,MnSO_4 + 2\,H_2SO_4 + 3\,H_2O$$

In a similar way chromic acid may be reduced to chromium sulphate. This reducing action, in the presence of water, probably explains the bleaching action of sulphur dioxide in some cases. The coloring matter is reduced, thus decolorizing the substance. In other cases, the sulphur dioxide unites directly with the coloring matter, producing a colorless compound. The color of materials bleached by sulphur dioxide will often return on exposure to the air, as in the case of straw. Bleaching by chlorine is more permanent.

212. Uses. — Great quantities of sulphur dioxide or of sulphites are used in the *bleaching* of many organic coloring matters. Straw, silk, wool, and other materials, which would be injured by chlorine, are decolorized by sulphur dioxide (Fig. 59). Cherries are sometimes bleached with sulphurous acid and then colored with the bright shades that are seen in the canned goods of commerce.

FIG. 59. — A CARNATION IN AIR (*a*) AND IN SULPHUR DIOXIDE (*b*).

Sulphur dioxide is sometimes used as a *disinfectant.* For this purpose, sulphur is burned, or liquid sulphur dioxide is allowed to evaporate in the room to be disin-

fected. In either case, the room should be tightly closed and the air in the room be kept moist, so that the disease germs may be killed by the sulphurous acid formed. This power of sulphurous acid to kill lower organisms is the reason for its use in the *curing* of wine and beer. The growth of mold is thus prevented. An increasing but questionable use of the acid is its employment as a food preservative. Sulphur dioxide not only attacks lower organisms, but is decidedly injurious to higher forms of life. Vegetable growth is blighted in the neighborhood of smelters and chemical works where the gas is generated. In cities, the gases from the burning of coal containing sulphur have a like effect.

The most important use of sulphur dioxide, however, is in the *manufacture of sulphuric acid*. Immense quantities are used for this purpose.

SULPHUR TRIOXIDE

213. Preparation. — Sulphur trioxide is prepared by the oxidation of sulphur dioxide. It is formed in small quantities when sulphur burns, and its presence causes the cloudiness often observed in sulphur dioxide. This oxidation may be made more rapid by the presence of catalytic agents. Finely divided platinum and ferric oxide are the more important ones. Platinized asbestos is prepared by soaking asbestos in platinum chloride and heating until finely divided platinum is left on the asbestos. A mixture of sulphur dioxide and air is passed over platinized asbestos (Fig. 60) and sulphur trioxide is formed. The temperature must be carefully regulated, as the trioxide decomposes at a temperature only a little higher than that necessary for its formation. The reaction is then reversible and may be represented:

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$$

214. Solubility. — Sulphur trioxide (sulphuric anhydride) dissolves in water, forming sulphuric acid:

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

As produced by the contact process, however, sulphur trioxide is not readily soluble in water. It is much more soluble in concentrated sulphuric acid, with which it forms a complex compound, called fuming sulphuric acid, $H_2SO_4 \cdot SO_3$.

$$H_2SO_4 + SO_3 \longrightarrow H_2SO_4 \cdot SO_3$$

SULPHURIC ACID

215. Preparation by Contact Process. — The experimental preparation of sulphur trioxide and sulphuric acid by the

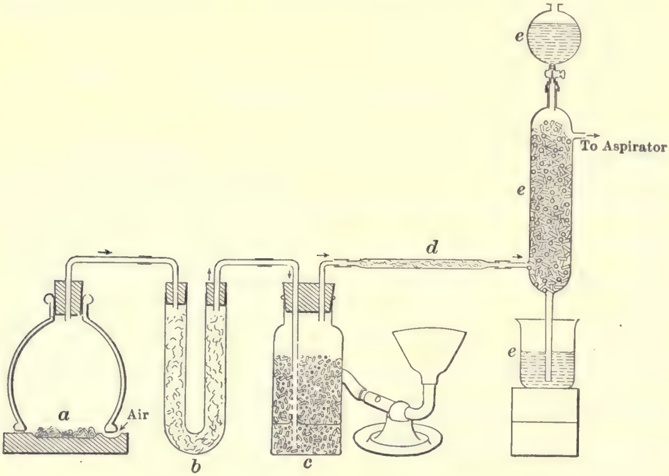


FIG. 60. — LABORATORY PREPARATION OF SULPHUR TRIOXIDE.

contact method is represented in Fig. 60. Sulphur (a) burns in the air drawn into the apparatus by an aspirator, and the sulphur dioxide formed passes with the excess of air into the U-tube (b) which is filled with some

loose material to rid the gases of sulphur dust. In the bottle (*c*) the gases lose their moisture as they make their way through the glass beads drenched with concentrated sulphuric acid. The platinized asbestos in the tube (*d*) is gently heated, and brings about the union of the sulphur dioxide with the oxygen of the air. The sulphur trioxide resulting from the action is absorbed by concentrated sulphuric acid trickling down through the apparatus (*e*). Water may be used for this last absorption, but is not nearly so efficient.

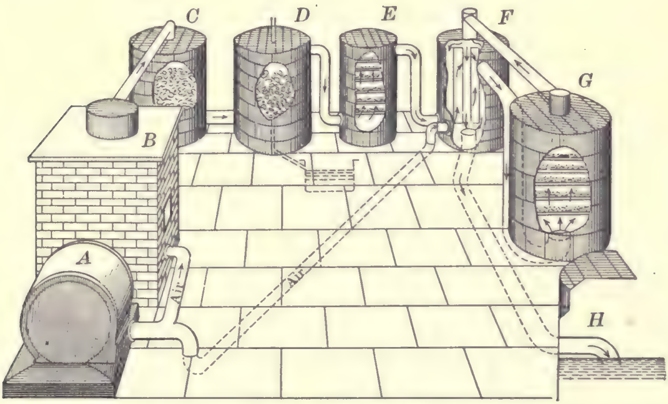


FIG. 61. — CONTACT PROCESS (DIAGRAMMATIC).

A, blower; *B*, pyrites burner; *C*, dry scrubber filled with coke; *D*, wet scrubber filled with coke wet with sulphuric acid; *E*, arsenic purifier; *F*, heater; *G*, contact chamber; *H*, absorber (concentrated sulphuric acid).

Pure concentrated sulphuric acid is prepared commercially from sulphur trioxide made by the method just stated. Sulphur, or ores containing sulphur, is burned in a furnace with air (Fig. 61, *B*). The sulphur dioxide and the other gaseous products of combustion are cooled, and freed from dust (*C*, *D*), arsenic (*E*), and most of the

moisture; the purified gases are then mixed with air (*F*) and passed through a tube (*G*) containing a catalytic agent, usually finely divided platinum. Unless the impurities are removed, they act on the platinum and it soon loses its catalytic power. The oxygen of the air combines with the sulphur dioxide and forms the trioxide:

$$2\ SO_2 + O_2 \longrightarrow 2\ SO_3$$

The sulphur trioxide is passed into concentrated sulphuric acid, and the solution is then diluted:

$$H_2SO_4 + SO_3 \longrightarrow H_2SO_4 \cdot SO_3$$
$$H_2SO_4 \cdot SO_3 + H_2O \longrightarrow 2\ H_2SO_4$$

216. Preparation by Chamber Process. — For more than a century, all of the sulphuric acid used for commercial purposes was made by the chamber process. To-day, owing to patents on the most approved forms of apparatus for carrying on the contact process, and to the fact that manufacturers dislike to abandon expensive equipment in good working order, the chamber process is still very extensively used for the manufacture of commercial oil of vitriol. The commercial acid produced by this process is not pure and is not concentrated. It contains only about 60% to 70% of sulphuric acid. The advantage of the contact process over the chamber process is that the former directly produces a pure, concentrated acid.

The sulphur dioxide used in the manufacture of sulphuric acid is often obtained by heating in contact with air some sulphide of a metal, usually iron sulphide, FeS_2, (pyrites). The sulphur dioxide is converted into the higher oxide by making use of nitrogen peroxide. The peroxide is obtained by the action of air with nitric oxide:

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

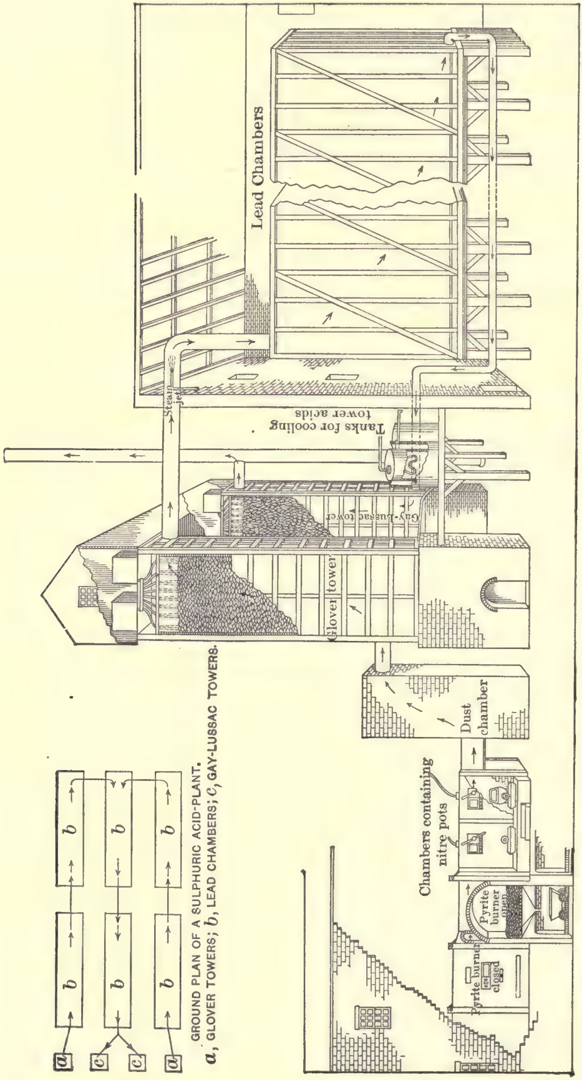
The nitric oxide results from the reaction of nitric acid with water and sulphur dioxide. The nitric acid is made by the action of sulphuric acid with sodium nitrate in vessels called niter pots:

$$2\,NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HNO_3$$
$$2\,HNO_3 + 3\,SO_2 + 2\,H_2O \longrightarrow 3\,H_2SO_4 + 2\,NO$$

Sulphur dioxide mixed with nitrogen peroxide is passed through a tower called the Glover tower (Fig. 62), to be described later, and then into large lead chambers. Within the chambers sulphur dioxide, nitric oxide, air, and steam are brought together. Complicated reactions take place which are not well understood.

Since approximately four fifths of the air is nitrogen, it is necessary to provide for the escape of the nitrogen and at the same time prevent the escape of the oxides of nitrogen as far as possible. This is accomplished by causing the chamber gases to pass through the Gay-Lussac tower. The tower is filled with coke. Concentrated sulphuric acid (78 % H_2SO_4) is conveyed to the top of the tower and sprinkled on the coke. The chamber gases enter the tower at the bottom and ascend against the stream of sulphuric acid as it trickles down. When the plant is running properly, practically all of the oxides of nitrogen are dissolved in the sulphuric acid. In this manner they are caught in the Gay-Lussac tower, while the nitrogen, being insoluble in the acid, escapes.

From the bottom of the Gay-Lussac tower, the sulphuric acid, carrying in solution the oxides of nitrogen, is pumped to a tank on the top of another tower, called the Glover tower, situated between the ore roasters and the chambers. The Glover tower is similar in construction to the Gay-Lussac tower. It is filled with lumps of quartz. At the



GROUND PLAN OF A SULPHURIC ACID-PLANT.
a, GLOVER TOWERS; b, LEAD CHAMBERS; c, GAY-LUSSAC TOWERS.

FIG. 62.—CHAMBER PROCESS FOR MAKING SULPHURIC ACID.

top of the tower are two tanks, one containing the liquid coming from the Gay-Lussac tower, and the other the chamber acid (55% H_2SO_4). As a mixture of these two liquids passes down through the Glover tower, it meets the hot gases coming from the ore roasters and from the nitric acid plant, on their way to the lead chambers. The result is that the dilute chamber acid is made more concentrated, the Gay-Lussac acid is decomposed by the water in the chamber acid, and the gases are allowed to enter the chambers, while sulphuric acid (67%) is obtained from the bottom of the tower. This chamber acid can be concentrated by boiling in iron and then in platinum pans, but for many commercial purposes needs no further treatment.

217. Physical Properties. — Sulphuric acid is a heavy, oily liquid. Ordinary commercial sulphuric acid, called *oil of vitriol*, is nearly twice as heavy as water. It boils at a higher temperature (338°) than most of the common acids, and many of its uses depend on this fact.

CHEMICAL PROPERTIES

218. Action with Water. — Sulphuric acid mixes with water in all proportions; during the mixing considerable heat is evolved. If such a mixture is made, *the acid should be slowly poured into the water, with constant stirring.* By doing this, the heat generated is distributed throughout the large mass of water, and the sudden generation of steam, which would cause spattering, is avoided. It is not advisable to use a glass vessel for mixing sulphuric acid and water.

219. Dehydrating Action. — Concentrated sulphuric acid absorbs moisture from the air, and this tendency of the acid to take up water explains many of its actions. Wood,

paper, sugar, and similar substances, containing hydrogen and oxygen, are charred by sulphuric acid. The acid removes the hydrogen and oxygen as water, leaving a residue consisting largely of carbon. On the flesh it acts similarly, and a painful wound results.

220. Action with Metals. — With metals the acid acts in two ways. If the action takes place at a low temperature, hydrogen may be evolved, provided sufficient water is present to dissolve the metallic sulphate formed:

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$
$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

Mercury, silver, and copper are not acted on by the cold acid, but if concentrated acid is used and the temperature raised sufficiently, these metals react, reducing part of the sulphuric acid, forming sulphur dioxide, water, and metallic sulphates (§ 206):

$$Cu + 2\ H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2\ H_2O$$

Thus at ordinary temperatures dilute sulphuric acid may act like hydrochloric acid, exchanging its hydrogen for metals, but when *hot and concentrated, it acts as an oxidizing agent.*

221. Action with Bases. — With bases and metallic oxides it reacts, forming water and sulphates:

$$2\ KOH + H_2SO_4 \longrightarrow 2\ H_2O + K_2SO_4$$
$$Ca(OH)_2 + H_2SO_4 \longrightarrow 2\ H_2O + CaSO_4$$
$$ZnO + H_2SO_4 \longrightarrow H_2O + ZnSO_4$$
$$Fe_2O_3 + 3\ H_2SO_4 \longrightarrow 3\ H_2O + Fe_2(SO_4)_3$$

222. Test for a Sulphate. — The sulphates are all soluble except four, the sulphates of barium, strontium, calcium,

and lead. In detecting the SO_4^{--} ion, a solution of barium chloride is usually employed. Representing by M^{++} any ion carrying two positive charges:

$$M^{++}SO_4^{--} + Ba^{++}(Cl^-)_2 \longrightarrow BaSO_4 + M^{++}(Cl^-)_2$$

The barium sulphate is easily identified, because it is white and insoluble in water, dilute acids, and alkalies. If, therefore, on adding barium chloride, a white precipitate, which is insoluble in hydrochloric acid, is obtained, the presence of sulphate ions is indicated.

223. Uses of Sulphuric Acid. — The absorption of water by sulphuric acid renders it a good dehydrating agent, and in the laboratory, gases are dried by being made to bubble through it (Fig. 22). In the manufacture of sulphuric acid, the air and sulphur dioxide employed are dried by contact with sulphuric acid. In the purification of petroleum products, kerosene, etc., it is used to remove, by charring, materials that would give offensive odors in burning. In the preparation of nitroglycerine, it aids the reaction by absorbing water.

As sulphuric acid has a higher boiling point than many acids, it is used in their preparation. Examples of this action have already been studied (§§ 82, 200).

On account of the conductivity of its solutions, sulphuric acid is used in electric batteries and in plating. It is used also as a catalytic agent in the production of glucose from starch and water.

It is used to dissolve the surface deposit on metals, previous to tinning or galvanizing. This process is called "pickling," and is essential if a firmly adherent coating is to be secured. A very important use is the conversion of certain insoluble phosphate rocks into soluble calcium phosphates, for use as fertilizers. Enormous quantities

of it are used in these operations, and in hundreds of others. *There are few materials in common use by civilized man with which sulphuric acid has not been directly or indirectly connected.*

SUMMARY

Sulphur dioxide can be prepared in several ways: direct combination of oxygen with free sulphur or with sulphur in sulphides; reduction of sulphuric acid; decomposition of sulphites with acids.

The characteristic odor, the weight, and the solubility in water of sulphur dioxide are three striking **physical properties**. **Chemically** it is an acid anhydride, forming sulphurous acid, which is a powerful reducing agent.

Sulphur dioxide is **used** in bleaching, as a disinfectant, as a food preservative, and, most important of all, in the manufacture of sulphuric acid.

An anhydride is an oxide that unites with water to form an acid or a base. An acid anhydride is named from the acid that it forms with water.

Sulphur trioxide is prepared by the oxidation of sulphur dioxide by means of a catalytic agent.

Sulphur trioxide is the **anhydride of sulphuric acid**. It combines energetically with water.

Sulphuric acid may be manufactured by the "contact process," consisting of the following steps:

(1) oxidation of sulphur to the dioxide;
(2) catalytic oxidation of the sulphur dioxide to the trioxide;
(3) dissolving the trioxide in concentrated sulphuric acid;
(4) dilution of the trioxide solution.

Sulphuric acid is a heavy, oily liquid of **high boiling point**.

With metals sulphuric acid acts in two ways. At low temperatures and when dilute, hydrogen may be evolved and the sulphate

of the metal formed. When hot and concentrated, it reacts with certain metals as an oxidizing agent, forming sulphur dioxide, water, and metallic sulphates. Sulphuric acid acts with bases and metallic oxides as a typical acid, forming water and a sulphate.

Sulphuric acid is **used** as a dehydrating agent; in the preparation of other acids; and in a wide range of industrial applications.

All common **sulphates** are soluble in water, except those of lead, barium, strontium, and calcium. To **test for a sulphate**, add a solution of barium chloride; a white, granular precipitate, insoluble in dilute hydrochloric acid, indicates the presence of sulphate ions.

EXERCISES

1. Which of the laboratory methods would you use for preparing *pure* sulphur dioxide? Why?

2. How many liters (standard conditions) of sulphur dioxide would result from the reaction of 12 grams of copper with concentrated sulphuric acid?

3. What weight of sodium sulphite must be decomposed to furnish 3.5 liters sulphur dioxide (standard conditions)?

4. What advantages has sulphur dioxide over chlorine as a bleaching agent? What disadvantage?

5. Compare the chemical actions in chlorine and sulphur dioxide bleaching.

6. What is an acid anhydride? Name two anhydrides containing sulphur, and give their formulas.

7. Describe the manufacture of sulphuric acid by the contact process.

8. How many pounds of sulphuric acid could be manufactured from 120 pounds of pure sulphur?

9. If a bottle partly filled with concentrated sulphuric acid is left open to the air, the liquid contents increase. Explain.

10. Calculate how many grams (*a*) of silver sulphate and (*b*) of copper sulphate you could make from a dime which is 10 % copper. A dime weighs 2.48 grams.

11. Explain why concentrated sulphuric acid must be poured slowly *into water* when the two liquids are mixed.

12. Account for the darkened rings formed on wood where bottles of concentrated sulphuric acid have been standing.

13. Why can either hydrochloric or sulphuric acid be used in the preparation of hydrogen sulphide? Which of these two acids must be taken for the preparation of nitric acid. Why?

14. Explain why boiling concentrated sulphuric acid produces such frightful burns.

15. Show how hot, concentrated sulphuric acid acts as an oxidizing agent with metallic silver.

16. What effect would you expect if a strip of lead were placed in dilute sulphuric acid? Explain.

17. Why is a dish containing sulphuric acid put inside the case of a delicate balance? Why are clocks for keeping exact time similarly treated?

18. Why is the civilization of a country said to be indicated by the amount of sulphuric acid it uses?

19. What is oil of vitriol? A dehydrating agent? Pickling a metal?

20. What chemical tests would you make to prove a given solution contained a sulphate of sodium?

CHAPTER XXI

NITROGEN AND THE ATMOSPHERE

224. Occurrence. — Nitrogen has already been mentioned as constituting a large portion of the atmosphere. It is found in a few mineral compounds, most of which, however, are the result of the activity of animal and vegetable organisms. Nitrogenous organic compounds exist in great variety; and one class, the proteins, of which the white of egg is an example, are directly concerned with the life processes. In fact, nitrogen is perhaps the most characteristic element in living organisms, since protein makes up the living matter of the muscles and the protoplasm of the cells. Life without nitrogen would be impossible.

225. Preparation. — Nitrogen may be prepared from air by causing the oxygen to combine with phosphorus in the presence of water. Phosphorus is employed because its great tendency to combine with oxygen insures the completeness of the reaction, even at ordinary temperatures, and because its oxides have a great tendency to combine with water and so are rapidly removed from the gas.

Other reducing agents may be used, provided the oxide formed is easily separated from the nitrogen. If air is passed through a strongly heated tube containing reduced copper or fine-meshed copper gauze, nearly pure nitrogen results (Figs. 63 and 64). The reason for the use of copper is that its oxide is a non-volatile solid. Nitrogen

prepared from air always contains argon and other impurities.

The oxidation of ammonia is a convenient method for preparing pure nitrogen. Ammonia gas is passed over strongly heated copper oxide. The hydrogen is oxidized to water, and the nitrogen remains. Heat alone will liberate nitrogen from some of its compounds. Ammonium nitrite, gently heated, decomposes into water and nitrogen. Owing to the unstable nature of ammonium nitrite, a mixture of ammonium chloride and sodium nitrite is used:

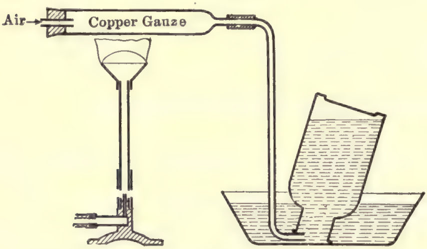


FIG. 63. — PREPARATION OF NITROGEN.

$$NH_4Cl + NaNO_2 \longrightarrow NaCl + NH_4NO_2$$
$$NH_4NO_2 \longrightarrow N_2 + 2\ H_2O$$

226. Physical Properties. — Nitrogen is slightly lighter than air, as we should expect from the fact that oxygen, the other chief constituent, is heavier. It is without color, odor, or taste. Nitrogen is less soluble in water than oxygen, so that the bubbles of gas given off, when ordinary water is warmed, contain a smaller proportion of nitrogen than air. Cooled to a very low temperature under pressure, nitrogen becomes a colorless liquid. This liquefaction is used commercially in the preparation of both oxygen and nitrogen from the air. The nitrogen of liquid air boils off before the oxygen, because the nitrogen has a lower boiling point. On further cooling, the liquid nitrogen freezes to a white solid.

CHEMICAL PROPERTIES

227. Inactivity. — The large amount of nitrogen in the air is due to its inertness; it does not combine readily with many substances, and its compounds are easily decomposed. The bulbs of some incandescent lamps contain nitrogen. It unites directly with few elements and with these only at high temperatures; sometimes the electric spark is necessary to cause combination. The ease and violence with which its compounds decompose is well illustrated by nitroglycerine and guncotton.

While nitrogen does not react readily, many reactions are affected by its presence. Thus burning cannot be so vigorous in air as in oxygen, since the large proportion of nitrogen dilutes the oxygen, preventing a rapid contact with the combustible material. Some heat is also employed in raising the temperature of the nitrogen; the temperature of combustion is lower than would be the case were nitrogen absent.

228. Action with Oxygen. — Nitrogen may be caused to combine slowly with oxygen by passing electric sparks through the mixture and removing the oxides by dissolving them in water as fast as they are formed. If they were not so removed, they would be decomposed by the heat of the succeeding sparks. Nitrogen will not burn in oxygen without a continual supply of external energy, as the temperature of the combustion is lower than the kindling point of nitrogen.

229. Action with Hydrogen. — Ammonia (NH_3) can be formed by the passage of sparks through a mixture of hydrogen and nitrogen, or by employing a catalytic agent. In this case, as in the similar production of the oxide, the

ammonia must be removed as formed, since the reaction is reversible and a point of equilibrium is reached, at which it proceeds as rapidly in one direction as in the other:

$$N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$$

230. Nitrides. — A number of nitrides are known; they are made by heating the metal with nitrogen. Aluminum nitride is at present the most important. It reacts with water:

$$AlN + 3\ H_2O \longrightarrow Al(OH)_3 + NH_3$$

If calcium carbide is heated with nitrogen, they combine, forming calcium cyanamid:

$$CaC_2 + N_2 \longrightarrow CaN_2C + C$$

This is valuable as a fertilizer and as a source of ammonia:

$$CaN_2C + 3\ H_2O \longrightarrow CaCO_3 + 2\ NH_3$$

231. Composition of the Air. — The average proportions of the chief constituents of the air are as follows:

	Composition	
	By volume	By weight
Nitrogen	78.06	75.5
Oxygen	21.00	23.2
Argon	0.94	1.3
Carbon dioxide . .	0.04	0.05

Traces of other substances are often present, but under the term *air* we usually include only the nitrogen, oxygen, and argon. The relative amounts of these are practically constant, except in certain localities, as in cities, and in poorly ventilated places.

The molecular motion of the gases, and the winds suffice to keep the composition of the atmosphere practically

constant. Local conditions may slightly affect the composition, especially in ill-ventilated places, but the total quantity of the air is so great — 15 pounds resting on each square inch of the earth — that even a large city produces scarcely any noticeable effect on the composition.

The constituents of air may be successively removed, so as to leave the nitrogen, by the apparatus represented in Fig. 64. The bottle (*a*) serves as an aspirator to draw air through the apparatus and also to collect the residual nitrogen. The oxygen is removed by combining it with copper (gauze) in the hard glass tube (*c*), which is heated by the combustion furnace (*b*). Before reaching the com-

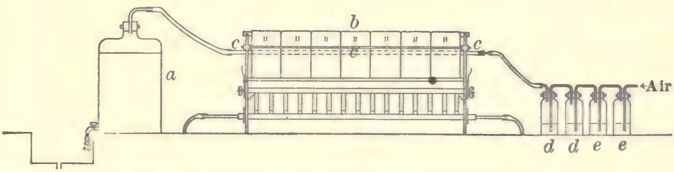


FIG. 64. — SEPARATION OF THE COMPONENTS OF AIR.

bustion tube, however, the air has to pass through the bottles (*ee*) containing a concentrated solution of potassium hydroxide to take out the carbon dioxide, and through the bottles (*dd*) containing concentrated sulphuric acid to remove the water vapor and ammonia. The nitrogen collected in (*a*) is purer than that obtained by method shown in Fig. 62.

232. Air is a Mixture. — Air was once regarded as an element; even now it is customary to refer to it as a single substance. Air differs from a compound in several important particulars.

(1) If air is cooled under pressure, it is found that the oxygen liquefies before the nitrogen, and, conversely, if the

liquid air is allowed to evaporate, the nitrogen vaporizes more rapidly than the oxygen. If air were a compound, it would have a definite boiling point, at which it would vaporize unchanged.

(2) If air is allowed to pass through an unglazed porcelain tube, it is found that the lighter nitrogen passes through the porcelain walls more rapidly than the oxygen; were they combined in molecules of a compound, they would go through with equal velocities.

(3) When air is brought in contact with water, nitrogen and oxygen dissolve in the proportion of 63 : 34; while in atmospheric air the proportion is about 4 : 1 by volume.

(4) If oxygen and nitrogen are mixed in the proportion in which they are found in the atmosphere, there is no evidence of reaction. We have found that when a chemical change takes place, there is usually a change in the temperature caused by the absorption or liberation of heat. Other energy changes, such as the production of light and sound (explosions), often accompany reactions. None of these energy changes occur in this case, hence there is no probability of a reaction.

(5) The composition is not absolutely uniform. While the differences in composition are slight, they are greater than those found in different samples of a chemical compound.

233. Water Vapor of the Air. — Some water vapor, derived from evaporation, is always present in the air; the amount usually increases with the temperature; thus warm breezes blowing over bodies of water are moist. When cooled, the vapor may condense as fog or rain. The air in desert regions, though warm, is dry, because the air before being warmed has passed over a cool, mountainous region and has deposited its moisture.

The amount of water in the air, relative to the amount necessary to saturate the air under given conditions, is known as the *relative humidity*. This is high when the air is nearly saturated, and low when the air is very dry.

If the air is warm, evaporation is hastened. If, however, the air is moist, evaporation, as from the skin and lungs, is retarded and we feel close, oppressed, and uncomfortable. If the air is dry, although warm, we note the cooling effect of the hastened evaporation. In cool weather we are still sensible to the moisture. Only a very small amount of water vapor is required to make a crisp, bracing atmosphere become clammy and disagreeable.

When the air is nearly half saturated, it is most comfortable. In crowded rooms it is usually too moist, and unfortunately there is no simple means by which the moisture in the room can be reduced. On a large scale moisture is most readily removed by cooling and condensing the water vapor.

234. Carbon Dioxide and Nitrogen Cycles. — Carbon dioxide is always present in the air, though in a very small proportion. In normal outdoor air about 4 parts in 10,000, or four hundredths of 1%, are present. The proportion may rise rather high in a crowded room from the exhalations of the people present. Carbon dioxide is continually given off to the air in the exhalations of animals and in combustion, but as it is taken up from the air by plants, the amount in the air remains practically constant. The very small percentage of carbon dioxide in the air furnishes all the carbon needed for the growth of plants.

The oxygen in the air is removed by animals and replaced by plant life; thus the plant and animal life pre-

serve the balance, maintaining the atmosphere at a constant composition.

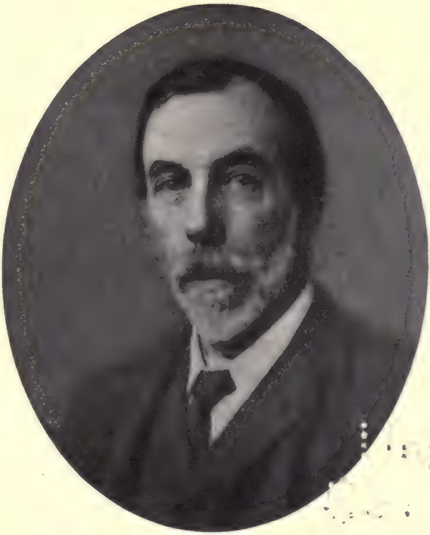
The nitrogen removed from the air to form soluble compounds in the soil, is taken up by plants and converted into proteins. These proteins are the source of the protoplasm of animals. These unstable proteins break up both during the life of the plants and animals and after their death, and the nitrogen finally makes its way back to the air.

235. Other Constituents of the Air. — Other materials are found in small amounts: argon, helium, and other inert gases (about 1%), traces of ammonia, sulphur compounds, and fine dust particles, which depend on local conditions and often produce climatic effects. These dust particles include a great variety of materials — steel, stone, soil, and coal dust. The organic particles include pollen grains and spores of plants, germs of disease, which are always present, shreds of various fabrics, as cotton and woolen cloth, and dried bits of refuse of all sorts.

THE INERT GASES

236. Discovery of Argon. — The discovery and investigation of the inert gases in the air have afforded one of the most brilliant and interesting chapters in the history of chemistry. In 1892 Rayleigh, an English scientist, noticed that nitrogen from the air was a trifle heavier than that obtained from nitrogen compounds. This meant that the supposedly pure nitrogen from the air contained some gas, heavier than nitrogen, which had remained undetected despite the careful study of the atmosphere for more than a century.

A small amount of the hitherto unknown gas was obtained by Ramsay, an English chemist, who passed nitrogen from the air over heated magnesium which com-



Sir William Ramsay was born in Glasgow, Scotland, in 1852. He shared with Rayleigh the honor of the discovery of argon. This element, although present in the atmosphere to the extent of about one per cent, had escaped detection because of its chemical inactivity. Ramsay is a remarkably skillful experimenter. Ramsay's other work has been to show the presence of other previously undiscovered gases in small amount in the atmosphere; to show that helium, formerly known only as a constituent of the sun, was given off by certain minerals; and to show, with Soddy, that helium is one of the decomposition products of radium. Ramsay was awarded the Nobel Prize in 1904.

bined with the nitrogen, forming magnesium nitride, a yellowish solid. This method yielded but a trace of the new gas, and a better way was soon devised by Lord Rayleigh. Even this improved method, however, was slow and many precautions were necessary, in order to secure a very small sample of the new material.

The new substance was found to constitute about 1% of the air. It is one fourth heavier than oxygen and over one third heavier than nitrogen. All attempts to make the gas enter into chemical combination failed, and hence it was given the name *argon*, signifying *inactive*.

237. Isolation of the Other Inert Gases. — Certain irregularities in the properties of argon led Rayleigh and Ramsay to suspect that this new gas was not itself pure. By means of liquid air the argon obtained from the atmosphere was liquefied, and, at the low temperatures obtained, repeated processes of fractional evaporation and liquefaction were carried on. The argon was found to contain minute amounts of other inert gases. Two of these could be separated only by using the extremely low temperature possible with liquid hydrogen. Three of the new inert gases were given names which bring to mind the long, baffling search for them. *Neon* means new; *xenon*, stranger; and *krypton*, hidden. Besides these three gases a trace of helium was found. This element was formerly supposed to exist only in the sun.

238. Properties. — Neon, xenon, krypton, and niton (§ 553) closely resemble argon, but each was found to have its *peculiar spectrum* and all except neon have a very low but *definite boiling point.* Thus they are elements and form a very closely related group with argon. Certain considerations have led us to believe that all these elements contain but one atom to the molecule. Their inertness

with respect to chemical combination explains why no compounds containing them are known, and why they were overlooked until recently.

239. Helium. — In 1869 Lockyer noticed some lines in the sun's spectrum which did not correspond with those of any element found on earth. In 1895 Ramsay, in searching for sources of argon, examined the gases given off by certain rare minerals when heated. In the case of clevite, a gas was obtained which gave a spectrum identical with that of the supposed element in the sun, and hence was given the name *helium.* The new element has since been obtained from the waters of certain mineral springs and has been found to exist in minute quantities in the atmosphere.

Helium is a very light gas, being only twice as heavy as hydrogen. Its properties resemble those of argon, and it is therefore classed with the other inert gases.

Recent researches have proved that helium results from the decomposition of radium, which is considered to be an element (see Chapter XL).

SUMMARY

Nitrogen constitutes the larger part of the air. It is a constituent of protoplasm and of proteins, hence is essential to vital processes.

It is **prepared** by

(1) the oxidation of ammonium compounds;

(2) removing the oxygen from the air by phosphorus; this is sufficiently pure for ordinary use.

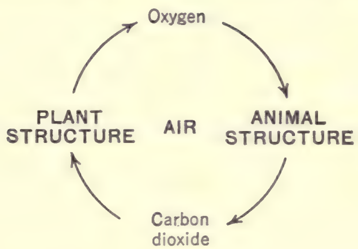
One liter of nitrogen weighs 1.26 grams. Its atomic weight is 14. The nitrogen molecule contains 2 atoms (N_2).

Nitrogen is generally **inert**; under electric stress it reacts slowly with oxygen and with hydrogen. A few bacteria are capable of assimilating it.

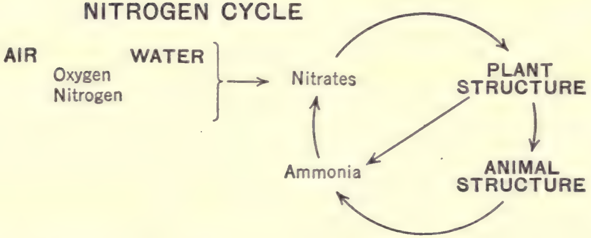
Air is essentially nitrogen, oxygen, and argon, with varying amounts of water vapor, carbon dioxide, and compounds of nitrogen and sulphur.

The amount of the air is so enormous that local conditions have little or no appreciable effect on its composition. The important factor determining the composition is the balance maintained between plant and animal life.

OXYGEN-CARBON DIOXIDE CYCLE



NITROGEN CYCLE



The **variation in composition** indicates that air is merely a mixture. Chemical reactions are always accompanied by thermal changes, and there are no such changes on mixing the constituents of air.

EXERCISES

1. Why are so few mineral compounds of nitrogen found in nature?

2. How was it shown that the material in the air, formerly known as nitrogen, was not a pure substance?

3. What chemical reactions take place in the air during a thunderstorm?

4. From what sources are the principal constituents of the air continually derived? By what means are they removed? Why is the composition of the air so nearly constant all over the earth?

5. What is the weight of air over a city lot 25 × 100 ft.? How much of it is oxygen?

6. State the ratio by volume of the two principal constituents of the air. How may this ratio be determined? Mention in regard to one of those constituents two important functions in nature.

7. Name four common substances present in the air. How could you show the presence of each?

8. Give two proofs that air is a mixture rather than a chemical compound. State how it could be proved by chemical means that air contains (*a*) water, (*b*) carbon dioxide.

9. Name four gases always present in the air. By what natural process is each removed from the air?

10. What change would take place if each of the following substances was left in an open vessel: (*a*) sodium, (*b*) anhydrous calcium chloride, (*c*) lime water, (*d*) crystals of washing soda, (*e*) concentrated sulphuric acid?

11. Name three of the rare and inert gases and state where they may be found. What peculiar property is shown by radium?

CHAPTER XXII

NITROGEN COMPOUNDS

AMMONIA

240. Natural Formation. — The most important constituent of all living organisms is protoplasm, a complex substance containing nitrogen, carbon, hydrogen, oxygen, and other elements. When a plant or animal dies and decomposition sets in, the protoplasm breaks up very quickly, yielding simpler compounds. The nitrogen unites with the hydrogen to form the gas ammonia (NH_3). The characteristic odor of ammonia can often be noted in the vicinity of heaps of decomposing animal or vegetable refuse.

241. Commercial Preparation. — Ammonia is obtained commercially as one of the products of the destructive distillation of coal, in the manufacture of coal gas and coke. Soft coal is heated in iron retorts at an intense heat. Moisture, volatile matter, and gases are driven off, and coke remains in the retort. The gases are cooled in pipes, and coal tar is extracted, then the gases are passed into a "scrubber," where they come in contact with water, and here the ammonia dissolves. The water containing ammonia compounds is boiled with milk of lime, and the expelled ammonia is passed into sulphuric acid; tarry materials are separated, and the solution of ammonium sulphate is evaporated and crystallized.

The dried, crystallized ammonium sulphate is mixed

with slaked lime in an iron retort and heated. Ammonia gas and water are given off, and calcium sulphate remains:

$$Ca(OH)_2 + (NH_4)_2SO_4 \rightleftarrows CaSO_4 + 2\,H_2O + 2\,NH_3$$

The ammonia may be dissolved in water, forming ammonia water, or spirits of hartshorn, or it may be dried by passing through quicklime (CaO) and compressed in tanks.

The possibility of utilizing the free nitrogen of the atmosphere in the manufacture of ammonia has appealed to many chemists. At present, two processes for accomplishing this bid fair to become of considerable commercial importance:

1. *Haber and Le Rossignol process.*

Nitrogen and hydrogen are caused to combine at a suitable temperature (500°–700° C.) and pressure (50–100 atmospheres) in the presence of a catalytic agent:

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$$

A state of equilibrium is reached when the gas mixture contains only a small per cent of ammonia. The ammonia is removed from the mixture, and the remainder, with a new mixture of hydrogen and nitrogen, is again passed through the apparatus.

2. *Ostwald process.*

Calcium cyanamid is prepared by passing nitrogen, obtained from air, over hot calcium carbide:

$$CaC_2 + N_2 \longrightarrow CaN_2C + C$$

The calcium cyanamid is then treated with steam under a pressure of from 6 to 8 atmospheres:

$$CaN_2C + 3\,H_2O \longrightarrow CaCO_3 + 2\,NH_3$$

242. Laboratory Preparation. — Ammonia is usually prepared (Fig. 65) by heating ammonium chloride (sal ammoniac) with calcium hydroxide (slaked lime):

$$Ca(OH)_2 + 2\,NH_4Cl \longrightarrow CaCl_2 + 2\,NH_3 + 2\,H_2O$$

In this preparation, any ammonium salt can be substituted for ammonium chloride, and any non-volatile base for the calcium hydroxide. A typical reaction probably proceeds as follows:

$$(NH_4)_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,NH_4OH$$
$$2\,NH_4OH \longrightarrow 2\,NH_3 + 2\,H_2O$$

the complete reaction being represented by the equation:

$$(NH_4)_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,NH_3 + 2\,H_2O$$

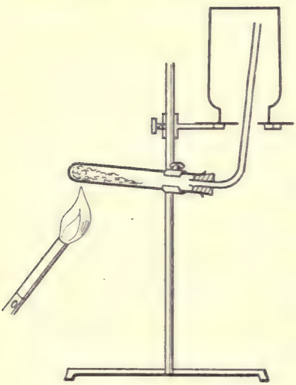


FIG. 65.

That is, ammonium hydroxide is first formed and breaks up at once into ammonia and water. Since ammonia is a gas, a volatile product can be formed as a result of the reaction between ammonium salts and bases. This is analogous to the fact that many acids are formed by the action of sulphuric acid upon their salts, because they have lower boiling points than sulphuric acid.

Ammonia can also be obtained by warming a strong ammonium hydroxide solution:

$$NH_4OH \longrightarrow NH_3 + H_2O$$

243. Physical Properties. — Ammonia is a colorless gas possessing a characteristic, pungent, overpowering odor.

It is lighter than air, and exceedingly soluble in water. At 0° C. one volume of water will hold in solution over 1000 volumes of the gas; at ordinary temperatures about 700 volumes. This solution is known as ammonia water, or ammonium hydroxide. On being heated or on standing exposed to air, it gives off ammonia.

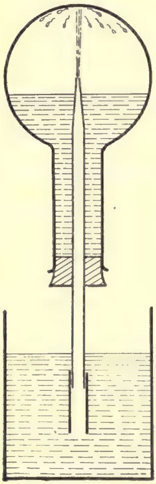


FIG. 66.

The great solubility of this gas is strikingly shown by the "ammonia fountain" (Fig. 66). A flask is filled with dry ammonia, and inverted over water. As soon as the ammonia comes in contact with the water, the gas rapidly dissolves and water rushes in, forming a fountain. Ammonia is easily liquefied; at ordinary temperatures a pressure of about 4.5 atmospheres is needed.

244. Chemical Properties. — Pure, dry ammonia is not an active substance; it is not readily combustible in air, but can be burned in oxygen. When ammonia is passed over heated copper oxide, water and nitrogen are obtained:

$$2\,NH_3 + 3\,CuO \longrightarrow 3\,Cu + 3\,H_2O + N_2$$

The most important chemical property of ammonia is the *basic character of its water solution.* This solution, which is often incorrectly called ammonia, turns red litmus blue, neutralizes acids, and conducts electricity; it behaves like a solution of a base. We may assume, therefore, the existence of OH^- ions in the solution of ammonia. When this solution is neutralized with hydrochloric acid, a salt is formed whose composition is represented by the formula NH_4Cl. Similar salts are formed with other

acids. The group NH_4 is known as the *ammonium radical.* A water solution of ammonia, then, contains the base ammonium hydroxide which reacts with acids to form salts:

$$NH_4OH + HCl \longrightarrow H_2O + NH_4Cl$$
$$2\,NH_4OH + H_2SO_4 \longrightarrow 2\,H_2O + (NH_4)_2SO_4$$

245. Ammonia Water. — Ammonia water contains both ammonia and ammonium hydroxide in solution; the ammonia, water, and ammonium hydroxide being in a state of equilibrium:

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

The alkaline properties of ammonia water are due to the fact that the ammonium hydroxide present dissociates, yielding hydroxyl (OH^-) ions:

$$NH_4OH \rightleftarrows NH_4^+ + OH^-$$

Ammonia water is commonly kept in rubber-stoppered bottles because concentrated solutions of ammonia cause cork to disintegrate rapidly, and they attack glass so as to make it difficult to remove a glass stopper without breaking the bottle.

The value of ammonia as a cleansing agent is due to its ability to dissolve grease. Its basic properties give it a use in the laboratory, whenever a volatile alkali is desirable. *Household ammonia* is prepared by adding, in quantity not to exceed 6%, oleic acid to ammonia water. Cloudy ammonias contain soap and frequently other ingredients.

246. Uses of Ammonia. — The most important uses of ammonia are as a refrigerating agent and for the preparation of ammonia water. When a gas is liquefied, heat is liberated, and when the liquid returns to the gaseous state, heat is absorbed. In one process for the manufacture of

artificial ice (Fig. 67), ammonia is compressed by powerful pumps; it is then cooled and liquefied by passing cold water over the pipes containing the compressed gas. The liquid ammonia is allowed to evaporate rapidly in pipes immersed in a concentrated solution of salt or calcium chloride. The ammonia in passing from the state of a liquid to that of a gas takes heat from the salt solution and cools it to a point below the freezing point of pure

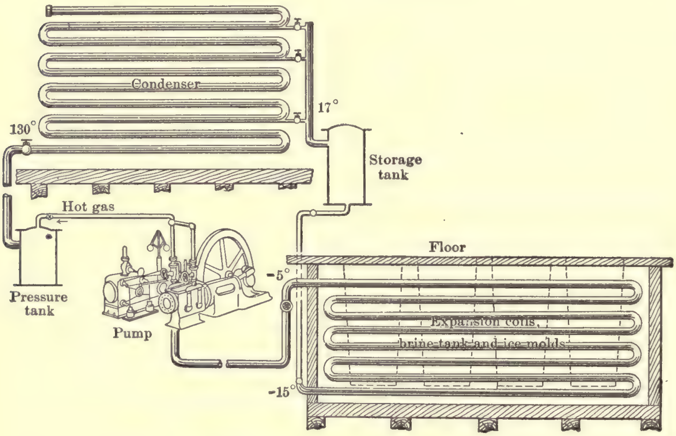


Fig. 67. — Refrigerating Plant.

water. Cans of water are placed in the cold brine, and the water is frozen in from 24 to 36 hours. Cold-storage rooms may be kept cool by distributing the cold brine to the apartments to be cooled, where it is passed through coils near the ceiling.

Large quantities of ammonia are used in the manufacture of sodium carbonate by the Solvay process.

247. Ammonium Salts. — Although ammonium has never been obtained in a free state, there are a large number of ammonium salts.

Ammonium salts react similarly to the compounds of sodium and potassium, and they may be considered as substances in which the group of atoms NH_4 (ammonium radical) takes the same part as an atom of hydrogen or potassium. Thus as potassium chloride dissociates into K^+ and Cl^- ions, ammonium chloride, NH_4Cl, dissociates into NH_4^+ and Cl^- ions.

If an electric current is passed through a solution of ammonium chloride, we might expect to obtain ammonium and chlorine, since these are the ions formed. The chlorine, however, liberated at the anode reacts with the ammonium salt present in the solution, forming hydrochloric acid and nitrogen. At the cathode, the NH_4^+ ion, on discharging, decomposes into ammonia and hydrogen, the ammonia dissolving in the water.

OXIDES OF NITROGEN

Nitrogen combines with oxygen in five proportions, corresponding to the formulas: N_2O, nitrous oxide; NO, nitric oxide; N_2O_3, nitrous anhydride; NO_2, nitrogen peroxide; N_2O_5, nitric anhydride.

248. Nitrous Oxide. — Nitrous oxide (N_2O), laughing gas, is prepared by heating ammonium nitrate (Fig. 68):

$$NH_4NO_3 \longrightarrow N_2O + 2\,H_2O$$

The nitrate melts and soon begins to decompose with effervescence. The heat must be carefully regulated or an explosion may occur. The nitrous oxide is a colorless gas with a slightly sweet taste. When inhaled, it produces unconsciousness and is used for this purpose in minor surgical operations. It was the first of modern anesthetics and was discovered by Sir Humphry Davy.

Nitrous oxide supports combustion almost as well as

oxygen, but, unlike oxygen, it does not react with nitric oxide, nor does it support the combustion of sulphur which is not burning vigorously.

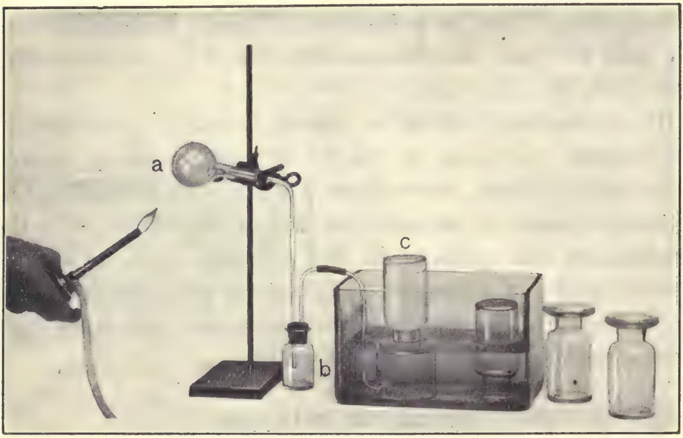


FIG. 68. — PREPARATION OF NITROUS OXIDE.

a, flask containing melted ammonium nitrate; *b*, catch bottle for water formed; *c*, collecting bottle.

249. Nitric Oxide. — Nitric oxide is a colorless gas; it is generally formed in the action of dilute nitric acid with metals. In the laboratory copper and nitric acid are used:

$$3\,Cu + 8\,HNO_3 \longrightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O$$

It does not support combustion, being more stable than nitrous oxide, but readily combines with oxygen, forming nitrogen peroxide, with a slight rise of temperature:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

This action makes it useful as a catalytic agent in the chamber process for the manufacture of sulphuric acid (§ 216).

250. Nitrogen Peroxide. — Nitrogen peroxide, NO_2, is a heavy red-brown gas of disagreeable odor. It is formed immediately whenever nitric oxide is brought in contact with oxygen or with air (Fig. 69). It dissolves in water, the solution has an acid reaction, and contains nitrous and nitric acids:

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

Thus the fumes from nitric acid, containing oxides of nitrogen, form nitric acid with water, and cause the corrosion usually observed on metal objects near which nitric acid is kept.

FIG. 69. — NITRIC OXIDE.
a, closed; *b*, open to air.

Nitrogen peroxide is readily liquefied and solidified, the liquid being yellow and the solid colorless. When the liquid vaporizes, the vapor given off at the boiling point is light brown and grows darker as the temperature rises. Vapor density determinations indicate that vapor given off from the liquid has a composition represented by the formula N_2O_4, part of the molecules of which *immediately* dissociate into NO_2 molecules, so that the light-colored gas is a mixture of the two oxides. As the temperature rises, more molecules dissociate, and the dark gas at high temperatures is chiefly NO_2. These changes are represented by the equation:

$$N_2O_4 \rightleftarrows NO_2 + NO_2$$

251. Other Oxides. — Nitrogen trioxide (N_2O_3) and nitrogen pentoxide (N_2O_5) are unstable substances of no

particular importance. They unite with water, forming nitrous and nitric acids:

$$H_2O + N_2O_3 \longrightarrow 2\,HNO_2$$
$$H_2O + N_2O_5 \longrightarrow 2\,HNO_3$$

Hence the trioxide is termed nitrous anhydride and the pentoxide is known as nitric anhydride.

NITRIC ACID

Nitric acid was known to the alchemists, who called it *aqua fortis* (strong water), because of the great chemical activity it displays. They prepared it by heating a mixture of potassium nitrate, copper sulphate, and potassium aluminum sulphate. The last two of these substances contain water of crystallization, and from this came the hydrogen which the acid contains.

252. Preparation from a Nitrate. — Both commercially and in the laboratory, nitric acid is prepared by heating a mixture of sulphuric acid and sodium nitrate. The latter substance is found in considerable quantities in certain parts of Chile and in the western United States. Other nitrates might be used; for instance, potassium nitrate, which is also found in nature, though in much smaller quantity than sodium nitrate.

The reaction may proceed in two stages. The first reaction is:

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

If there is an excess of acid and the temperature is kept low, the reaction does not proceed beyond this point. If, on the other hand, there is an excess of sodium nitrate, the sodium hydrogen sulphate that is formed in the first

action reacts at a higher temperature with more sodium nitrate, according to the equation:

$$NaNO_3 + NaHSO_4 \longrightarrow Na_2SO_4 + HNO_3$$

Writing one equation to show the final results of the two stages of the reaction, we have:

$$2\,NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HNO_3$$

Since the second action requires a higher temperature than the first, and since nitric acid undergoes considerable decomposition at the higher temperature, it is customary to use enough sulphuric acid to give only the first reaction. Sulphuric acid is used in this operation for the reason that its boiling point is higher than that of nitric acid. Very few acids could be substituted for sulphuric acid because most of them have too low boiling points. In the laboratory preparation of nitric acid, the distilled acid is usually collected in a test tube or other receiver, kept cool by water in a battery jar (*a*, Fig. 70).

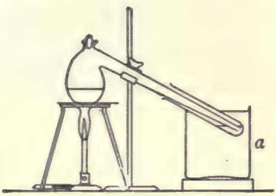
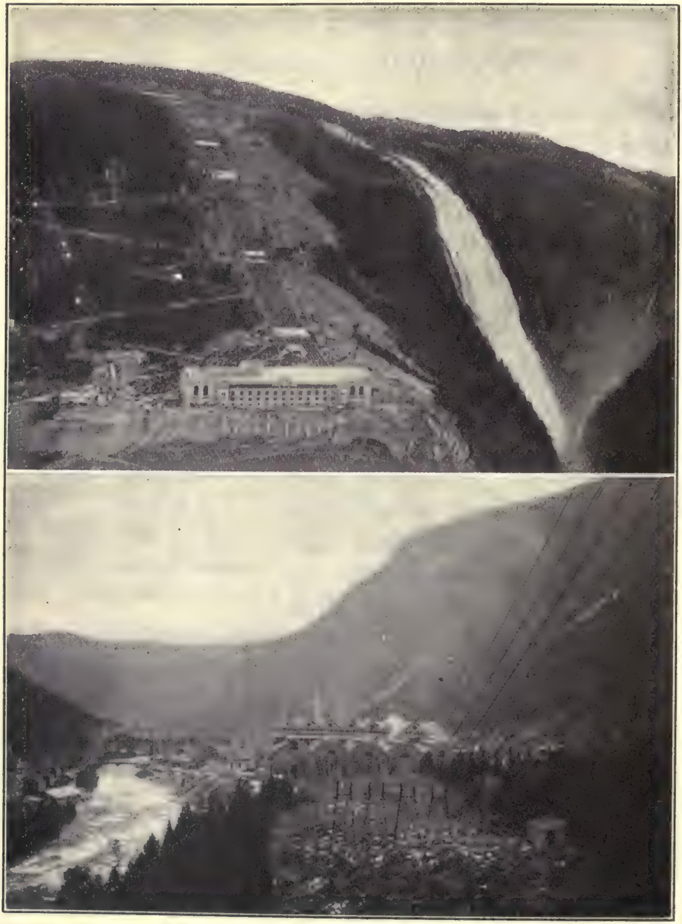


FIG. 70.

Nitric acid is an important article of commerce; so the reaction that has been described is carried out on a large scale. Iron retorts are used, and the acid is condensed and collected in a series of earthenware vessels.

253. Preparation from Air.—Several processes for employing atmospheric nitrogen in the manufacture of nitric acid are in use. A number of these utilize the direct oxidation of atmospheric nitrogen by high-tension arc discharges of electricity. Under suitable conditions, small quantities of nitric oxide are formed:



Courtesy of Norwegian Hydro-Electric Co., Rjuken.

FIG. 71. — ELECTRIC POWER HOUSE, RJUKEN, NORWAY (ABOVE), AND CHEMICAL PLANT (BELOW), WHERE THE ELECTRICITY IS USED IN THE FIXATION OF NITROGEN.

$$N_2 + O_2 \longrightarrow 2\,NO$$

Below 600° C., nitric oxide combines with oxygen to form nitrogen peroxide:

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

Nitrogen peroxide unites with water to form a mixture of nitric acid and nitrous acid:

$$2\,NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

Except in extremely dilute solutions, nitrous acid decomposes, yielding nitric acid, nitric oxide, and water:

$$3\,HNO_2 \longrightarrow HNO_3 + 2\,NO + H_2O$$

The final equation is

$$3\,N_2 + 6\,O_2 + 2\,H_2O \longrightarrow 4\,HNO_3 + 2\,NO$$

254. Physical Properties. — Nitric acid is a colorless liquid at ordinary temperatures. The diluted acid has boiling points varying with the dilution. A mixture that contains 68% of pure nitric acid boils constantly at 120°.

As it is ordinarily prepared, nitric acid contains considerable water and is colored yellow by the presence of dissolved oxides of nitrogen, which result from the decomposition of the acid by the heat used in its preparation. It is usual to distil the acid in an apparatus in which the pressure is less than that of the atmosphere. In this way the distillation can be carried on at a lower temperature and the undesirable decomposition is avoided.

255. Chemical Properties. — The chemical behavior of nitric acid is very interesting. Generally its action is not a simple one. This is because it possesses two distinct chemical characteristics, both of which it displays in a marked degree.

First, it is a *very strong acid*. This is because it is highly dissociated into ions when dissolved in water, even in concentrated solution. The hydrogen ions, being present in large numbers, produce all the actions that are characteristic of acids, such as the formation of salts with bases and the transference of the electric charge of the hydrogen ion to metallic atoms, forming metallic ions, when the acid is brought in contact with a metal.

Second, nitric acid is a *powerful oxidizing agent*. This can be shown in a number of ways: charcoal can be made to burn in nitric acid; horsehair will take fire if put into the gaseous substance; both the coloring matter and the fabric of cotton or woolen goods are quickly destroyed by it.

256. Reduction Products. — When nitric acid does oxidizing work, it is itself reduced. There are various reduction products of the acid. The product formed depends on a number of conditions, particularly on the temperature and the degree of dilution of the acid. In any case, there are several reduction products, though usually one is found in excess of the others. If the acid is moderately dilute, and acts at ordinary temperatures, the reduction product is commonly nitric oxide. From concentrated nitric acid, a large quantity of nitrogen peroxide is always obtained. From very dilute acid, the reduction product may be nitrous oxide, hydrogen, or even ammonia. Thus we see that the more dilute the acid, the farther the reduction is carried. This does not mean that the more dilute acid is the stronger oxidizing agent; on the contrary, it is because the concentrated acid is such a powerful oxidizing agent that the lower reduction products cannot escape from the acid without being themselves oxidized to a certain extent.

As we should expect from its being so strong an oxidiz-

ing agent, nitric acid is a rather unstable compound, tending to give up part of its oxygen to form more stable compounds. It will do this under the influence of light, or more readily if some oxidizable substance is present.

257. Action with Metals. — Nitric acid acts with many of the metals, but owing to its dual chemical character, it does not act on them in the same way that other acids do. Hydrogen is seldom evolved by the action of nitric acid on metals. The gases that are given off are the reduction products of nitric acid.

The action of moderately dilute nitric acid on copper may be taken as a type of its action on the heavy metals, as silver, mercury, and lead. Experiment shows that the products of this action are copper nitrate, nitric oxide, and water.

It is probable that, as a result of the first stage of the action, there is a tendency to liberate hydrogen, according to the equation:

$$(1) \qquad Cu + 2\,HNO_3 \longrightarrow Cu(NO_3)_2 + 2\,H$$

But the nascent hydrogen is at once oxidized to water by the nitric acid, and a part of the nitric acid is reduced to nitric oxide at the same time:

$$(2) \qquad 3\,H + HNO_3 \longrightarrow 2\,H_2O + NO$$

To combine equations (1) and (2), we should consider that only *two* atoms of hydrogen were produced in equation (1), while *three* atoms of hydrogen were consumed in equation (2). The hydrogen could not have been consumed more rapidly than it was produced. If it had been produced more rapidly than it was consumed, free hydrogen would have appeared. To satisfy these conditions,

we multiply equation (1) by 3, and equation (2) by 2, so that they become respectively:

$$3\ Cu + 6\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 6\ H$$

and

$$6\ H + 2\ HNO_3 \longrightarrow 4\ H_2O + 2\ NO$$

The sum of these latter equations is the equation usually written for the reaction between copper and cold, dilute nitric acid:

$$3\ Cu + 8\ HNO_3 \longrightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

The balancing of such an equation as this, involving oxidation and reduction, is a somewhat difficult matter. It will probably be found convenient to remember the numbers 3 and 8 in this reaction.

When concentrated nitric acid reacts with copper, nitrogen peroxide is formed in considerable quantity, as well as some nitric oxide:

$$Cu + 4\ HNO_3 \longrightarrow Cu(NO_3)_2 + 2\ NO_2 + 2\ H_2O$$

When very dilute nitric acid reacts with zinc, or metals similar to it, the nitrogen of the acid is reduced to ammonia, which then combines with more of the acid, forming ammonium nitrate:

$$4\ Zn + 10\ HNO_3 \longrightarrow 4\ Zn(NO_3)_2 + NH_4NO_3 + 3\ H_2O$$

258. Uses. — Nitric acid dissolves silver, but does not act on gold; hence it is sometimes used to separate these two metals. The chief uses of nitric acid depend upon its ability to form unstable salts with organic bases (compounds containing hydrogen and carbon). Two of these products are nitroglycerine and guncotton. Celluloid is a mixture of nitrocelluloses and camphor.

Aqua regia is a mixture of nitric and hydrochloric acids.

It dissolves gold and platinum. The fact that the mixture of the acids does what neither acting alone can do, is explained by the liberation of nascent chlorine by the interaction of the two acids. The hydrogen of the hydrochloric acid is oxidized by the nitric acid:

$$3\ HCl + HNO_3 \longrightarrow 3\ Cl + 2\ H_2O + NO$$

Nitric acid is also extensively used in the manufacture of many dyes and drugs.

NITRATES

259. Sodium and Potassium Nitrates. — The salts formed by the replacement of the hydrogen of nitric acid are called nitrates. The nitrates of sodium and potassium are the only ones found in nature in any considerable quantity. Potassium nitrate, ordinary saltpeter, is manufactured in a manner analogous to that by which it is produced in nature. In the presence of bases, nitrogenous organic matter decomposes under the influence of certain minute organisms called nitrifying bacteria, and has its nitrogen transformed into nitrates.

Sodium nitrate is found in large quantities in Chile, from which fact it gets the name *Chile saltpeter*. Nitric acid is made from it. Because of its great abundance, sodium nitrate is cheaper than potassium nitrate. The following reaction will take place in hot concentrated solution:

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

Advantage is taken of the fact to prepare the more expensive potassium nitrate (§ 185).

One of the chief uses of potassium nitrate is for the manufacture of gunpowder. It is also used as a preservative in the making of corned beef.

260. Calcium nitrate has become of importance on account of its production by the reaction between a solution of calcium hydroxide and nitrogen peroxide produced from the atmosphere by the use of electricity. Its chief use is in supplying combined nitrogen to the soil for plant food.

261. Preparation of Nitrates. — Nitrates, like the salts of the other common acids, can be made in several simple ways in the laboratory:

(*a*) By the action of nitric acid on metals:

$$3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + NO + 2\,H_2O$$

As has been pointed out, hydrogen is seldom a product in the action of nitric acid on metals.

(*b*) By the action of nitric acid on oxides or hydroxides of metals:

$$ZnO + 2\,HNO_3 \longrightarrow H_2O + Zn(NO_3)_2$$
$$Zn(OH)_2 + 2\,HNO_3 \longrightarrow 2\,H_2O + Zn(NO_3)_2$$

(*c*) By the action of nitric acid on salts that give a volatile product with this acid:

$$ZnCO_3 + 2\,HNO_3 \longrightarrow CO_2 + H_2O + Zn(NO_3)_2$$

Nitrates cannot be prepared by precipitation, because nitrates of all metals are soluble in water. This fact also prevents the use of a precipitation method as a test for a nitrate.

262. Test for Nitrates. — The test for the NO_3^- ion depends upon the oxidizing power of the NO_3 group. The substance to be tested is mixed with a solution of ferrous sulphate. Concentrated sulphuric acid is then added, so as to form a layer below the mixed solution. Nitric acid, in the presence of sulphuric acid, oxidizes ferrous sulphate

to ferric sulphate and, at the same time, nitric oxide, NO, is formed as a reduction product. This combines with some of the unchanged ferrous sulphate (Fig. 72, *a*), producing a characteristic unstable compound (whose formula may be $2\ FeSO_4 \cdot NO$), which appears as a dark coloration or ring (*b*) just above the heavier sulphuric acid (*c*).

FIG. 72.

All nitrates are decomposed by heat. The sodium and potassium salts, when thus treated, give up oxygen and are converted into nitrites. Other nitrates yield oxygen and nitrogen peroxide, and the oxide of a metal.

263. Fixation of Nitrogen. — Nitrogen compounds are invariably found in certain tissues of both plants and animals. The nitrogen which helps to form these compounds comes from the soil, since neither plants nor animals, with one exception about to be noted, can take nitrogen from the air. The problem how to maintain the supply of nitrogen compounds in the soil was somewhat difficult to solve. The natural renewal of nitrates takes place slowly, and the soils become infertile because of the lack of nitrogen compounds. This difficulty is usually overcome by manuring the fields, in which case the decomposing animal matter gives up its combined nitrogen to the soil and so to growing plants. Enormous quantities of nitrogenous farm products are consumed in cities, and most of the combined nitrogen contained in these is not returned to the soil.

Certain parasitic plants of microscopic size, called

nitrogen-fixing bacteria, found in the tubercles on the roots of leguminous plants, such as peas and clover (Fig. 73), have the power of taking nitrogen from the air and making it available to the plants. The nitrogen-fixing bacteria are of great importance in rendering productive soils that had remained infertile from the lack of nitrogen compounds. The process of converting nitrogen from the air into useful compounds is called the *fixation of nitrogen.* It is difficult to accomplish because of the inactive character of nitrogen. The fixation of nitrogen is brought about in nature to a small extent by the passage of lightning through air. The oxygen and nitrogen unite, forming nitrogen peroxide, which in turn forms nitric acid on dissolving in water. During a thunderstorm a certain amount of nitric acid is formed in this way.

FIG. 73.—BEAN ROOTS SHOWING NODULES.

The use of atmospheric nitrogen in the manufacture of ammonia, calcium cyanamid, and nitric acid has already been briefly described (§§ 229, 241, 253). These processes for the fixation of nitrogen are of great importance as a source of nitrogen for plant life.

Calcium cyanamid when added to the soil is soon converted into compounds that are soluble, and can be ab-

sorbed by the roots of plants. Ammonium compounds and nitrates are directly available as plant food.

264. Explosives. — Certain nitrogen compounds that contain carbon, oxygen, and hydrogen are so unstable that they decompose under the impulse of a slight shock, forming gaseous products. For this reason these compounds are powerful explosives. Nitroglycerine and guncotton are examples of this class of compounds. Nitroglycerine is made by treating glycerine, an organic base, with a mixture of nitric and sulphuric acids. The sulphuric acid serves to absorb the water that is formed by the reaction of the other two substances:

$$C_3H_5(OH)_3 + 3\,HNO_3 \longrightarrow 3\,H_2O + C_3H_5(NO_3)_3$$

The nitroglycerine molecule is evidently a very unstable one that can rearrange itself into new and more stable molecules under the impulse of a slight shock. Dynamite is a mixture of wood pulp, sodium nitrate,

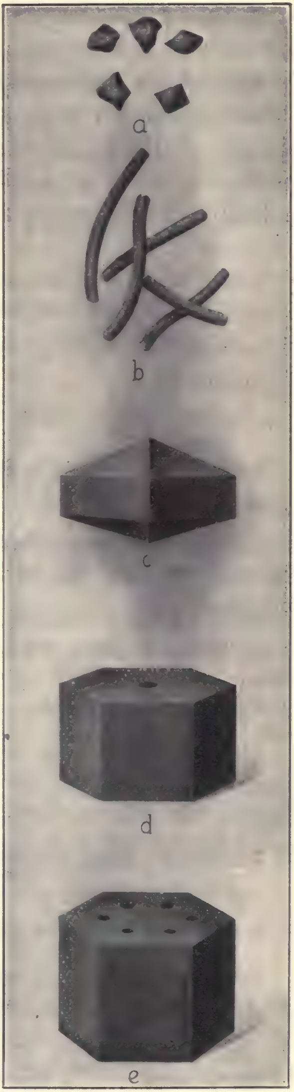


FIG. 74.

and nitroglycerine. Other inert material may be used in place of wood pulp.

Guncotton (nitrocellulose) is made by treating cotton fiber (cellulose) with a mixture of nitric and sulphuric acids. Cellulose, like glycerine, is an organic base, and nitrocellulose is an unstable salt. Smokeless powder is a mixture of guncotton and nitroglycerine, or similar substances.

Some forms of explosives containing nitrogen compounds are shown in Fig. 74: *a* is granular gunpowder; *b*, cordite; *c*, giant powder; *d*, brown prismatic powder; *e*, maximite.

SUMMARY

Ammonia is formed in nature as a decomposition product from protoplasm.

It is **obtained commercially** as a by-product from the distillation of coal. It may be produced by the action of a base on an ammonium salt.

Ammonia is a gas with a pungent odor; its specific gravity, relative to hydrogen, is 8.5. It is **very soluble** in water, 1 liter of water at 15° dissolves 720 liters of ammonia.

The solution is basic and contains NH_4^+ and OH^- ions. It reacts with acids with the formation of water and an ammonium salt.

Ammonia is **used** as a refrigerating agent, and in the preparation of sodium bicarbonate and of **ammonia water**.

Nitrogen forms five oxides.

Nitrous oxide, N_2O, is made by heating ammonium nitrate. It is a good supporter of combustion, and is used as an anesthetic ("laughing gas").

Nitric oxide, NO, is formed by the action of dilute nitric acid on metals. It unites with oxygen at ordinary temperatures, forming

nitrogen peroxide, NO_2. This is a brown, poisonous gas, soluble in water.

Nitrous anhydride, N_2O_3, and **nitric anhydride**, N_2O_5, are unimportant.

Nitric acid is prepared by the reaction between sulphuric acid and a nitrate.

When pure, it is a colorless liquid, with a specific gravity of 1.53.

It is a powerful **oxidizing agent**, and when it reacts with metals, the hydrogen is oxidized to water and reduction products are formed. A mixture of nitric and hydrochloric acid is ***aqua regia;*** this furnishes nascent chlorine.

Nitric acid is **used** in the preparation of nitrates and explosives.

The **nitrates** of sodium and potassium are the most important. Nitrates may be **prepared** by the action of nitric acid on:

(1) metals; (2) oxides or hydroxides; (3) salts yielding volatile products.

Potassium nitrate is **used** in gunpowder and as a meat preservative; sodium nitrate as a fertilizer and for the production of nitric acid and potassium nitrate.

Fixation of nitrogen is the conversion of the free nitrogen of the atmosphere into useful compounds.

It is brought about by chemical methods and by the use of nitrogen-fixing bacteria. These are processes that are of great importance in furnishing nitrogen to plants.

Nitrifying bacteria convert organic nitrogen compounds into ammonia, nitrites, and nitrates.

Many nitrogen compounds are used in **explosives**. Nitroglycerine and guncotton are made by the action of nitric acid on glycerine and cotton respectively. Dynamite is a mixture of inert materials with nitroglycerine.

EXERCISES

1. How many liters of ammonia can be obtained by the action of lime on 50 grams of ammonium chloride?

2. Why is ammonia called the volatile alkali?

3. What method would you use to get a few cubic centimeters of ammonia gas for use in the laboratory?

4. Explain what is meant by the ammonium theory.

5. Show how the nitrogen oxides illustrate the law of multiple proportions.

6. By what tests would you distinguish between oxygen and nitrous oxide?

7. What volume of air would convert 100 c.c. of nitric oxide, NO, into nitrogen peroxide, NO_2?

8. Compare nitric acid with sulphuric acid and with hydrochloric acid in regard to its action with metals.

9. Tell about the natural formation of (*a*) ammonia, (*b*) nitric acid, (*c*) nitrates.

10. Why is nitric acid a better solvent than hydrochloric acid for silver, mercury, and lead?

11. What is *aqua fortis? aqua regia? sal ammoniac?*

12. Upon what properties of nitric acid do most of its uses depend? Illustrate.

13. How would you test an unknown substance for the nitrate ion? For the ammonium ion?

14. Explain the significance of the statement, "No life without nitrogen."

15. State the substances and conditions necessary to yield each of the following products from nitrogen compounds: oxygen, hydrogen, nitric oxide, nitrogen peroxide.

16. Why has it become necessary to devote much attention to the artificial production of fertilizers containing nitrogen?

17. Describe a process for the fixation of nitrogen.

CHAPTER XXIII

ELEMENTS OF THE NITROGEN GROUP

265. General Characteristics. — The elements in this group resemble each other in properties to a considerable degree. It is approximately true that in going through the group a given property changes steadily in one direction as the atomic weights increase. Thus nitrogen is a colorless gas; phosphorus is a waxlike solid; arsenic is a dark gray solid with something of the appearance of a metal; antimony has a distinctly metallic appearance; bismuth is a metal. Their respective specific gravities are: 0.97,[1] 1.8, 5.7, 6.7, 9.7. There is a similar gradation of chemical properties from the non-metallic or acid-forming nitrogen and phosphorus, through the acid-forming but faintly metallic arsenic, to the metallic antimony and bismuth, which have but faint traces of acid character.

The elements of the family form many compounds similar in character and formula. All except bismuth form compounds of the type XH_3, where X stands for the symbol of any element in the family. There are two oxides, X_2O_3 and X_2O_5, which are the anhydrides of the acids HXO_2 and HXO_3 respectively. In the cases of phosphorus, arsenic, and antimony, the acid formulas are H_3XO_3 and H_3XO_4, showing the addition of three molecules of water to the anhydride instead of one.

$$X_2O_5 + H_2O \longrightarrow 2\ HXO_3$$
$$X_2O_5 + 3\ H_2O \longrightarrow 2\ H_3XO_4$$

[1] Air = 1; the other specific gravities refer to water.

PHOSPHORUS

266. Occurrence. — About one fourth of the bones and teeth of animals is calcium phosphate. Rock phosphates, containing calcium phosphate, $Ca_3(PO_4)_2$, derived from the bones of prehistoric animals, are the chief source of phosphorus. Complex phosphorus compounds are a small but very essential constituent of the muscles, nerves, and brains of animals. Soluble phosphates are very necessary for plant growth, and all vegetable foods contain a small per cent of phosphorus. Man derives his largest supply from such protein foods as beans, peas, cheese, oatmeal, meat, and bread.

Phosphorus was discovered in 1669 by Brand, an alchemist of Hamburg, while distilling urine in the course of his attempts to find the philosopher's stone. Scheele, the Swedish chemist, prepared it from bones in 1771.

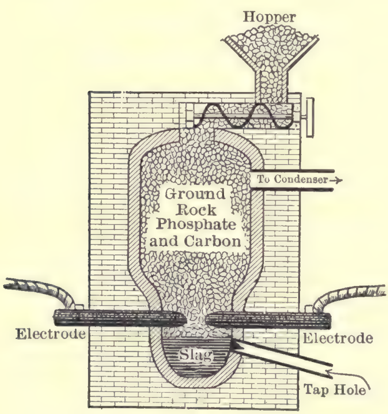


FIG. 75. — ELECTRIC FURNACE FOR PHOSPHORUS EXTRACTION.

267. Preparation. — Phosphorus is obtained by passing an electric current through a mixture of rock phosphates, sand (SiO_2), and coke, or anthracite coal. The finely ground materials are put in the hopper of the electric furnace (Fig. 75), and then drop upon the worm conveyor which feeds to the interior of the furnace. The resistance of the mixture to the passage of the current between the carbon electrodes

develops intense heat which brings about the following reaction :

$$Ca_3(PO_4)_2 + 3\ SiO_2 + 5\ C \longrightarrow 3\ CaSiO_3 + 5\ CO + 2\ P$$

The calcium silicate forms a slag which collects at the bottom of the furnace, where it is tapped off from time to time. The mixture of carbon monoxide and phosphorus vapors passes out to the condenser, where the phosphorus is condensed by water, and is run into cylindrical molds.

268. White Phosphorus. — Phosphorus exists in two well-known allotropic forms — the *white* and the *red.*

White phosphorus is a waxy, translucent solid which is a little less than twice as heavy as water. It melts easily (44° C.), but on account of its inflammability, the melting must be done under water. It is readily soluble in carbon disulphide. When this solution is made to evaporate slowly, with the exclusion of air, fine and almost colorless crystals of phosphorus are obtained.

White phosphorus is a spontaneously inflammable substance. It oxidizes slowly in air, and the heat produced raises the temperature of the phosphorus to its kindling point (35° C.). For this reason, the phosphorus is kept under water. Phosphorus burns in oxygen with a brilliant flame, producing dense white fumes of phosphorus pentoxide (Fig. 10).

$$4\ P + 5\ O_2 \longrightarrow 2\ P_2O_5$$

White phosphorus when oxidizing slowly glows in the dark and some ozone is produced. The odor of the latter substance (or possibly that of an oxide of phosphorus) has led to the common error that white phosphorus has an odor.

White phosphorus is so active that it combines readily

in the cold with halogens, and at a moderate heat with sulphur and the more energetic metallic elements.

269. Red Phosphorus. — When white phosphorus is heated to about 250° C. in a vessel from which air is excluded, red phosphorus is obtained. Light brings about this conversion at ordinary temperatures. This accounts for the change of color when white phosphorus is exposed to light. After a time a reddish coating may be observed. The change takes place more rapidly in a confined carbon disulphide solution exposed to light.

The change from white to red phosphorus results in the liberation of considerable heat. This indicates that red phosphorus is the more stable at ordinary temperatures, but is less active. Hence red phosphorus is less easily ignited and when burned evolves less heat than an equal weight of the white variety. In general, red phosphorus reacts less readily than the white form.

Red phosphorus is a soft, reddish powder which is slightly more than twice as heavy as water. It is insoluble not only in water, but *also* in carbon disulphide.

When red phosphorus is heated to about 290°, and the resulting vapors are suddenly cooled, the conversion of red to white phosphorus occurs. Thus we see that red and white phosphorus are allotropic forms comparable to those of sulphur. The red form is the stable form at all temperatures at which both forms are known, and contains less energy than the white variety. In other words, adding more energy to the red form converts it into the white variety.

270. Phosphorus Poisoning. — Red phosphorus is not poisonous, while white phosphorus is *so active a poison* that a minute quantity taken internally causes death.

Formerly in the making of matches, the workmen, by inhaling the phosphorus vapors, contracted a painful disease characterized by ulceration of the jawbones. Recently, however, legislation in this country (as is the case in practically all civilized nations of the world) has prohibited the use of poisonous white phosphorus in the manufacture of matches, and instead red phosphorus or a non-poisonous compound of phosphorus, known as phosphorus "sesquisulphide" (P_4S_3), is used.

The easily inflammable white phosphorus should never be handled except with tongs. Phosphorus burns are deep seated and very difficult to heal, even if suppuration does not occur. An alcohol solution of picric acid is effective in their treatment.

271. Uses. — Phosphorus is used in the manufacture of matches. *Phosphor bronze* contains from 0.2% to 4% of phosphorus, either in the form of the phosphide of copper or of the phosphide of tin. It is a hard, tenacious alloy which is not corroded by water. A minor use of phosphorus is as a constituent of poisonous pastes for rats and mice.

272. Matches. — A common *friction match* (Fig. 76) consists of a stick of soft wood, about half an inch of which has been dipped in melted paraffin, sulphur, or other easily ignitible material; and a "head" composed of a mixture of an oxidizing material (such as potassium chlorate or oxide of lead) phosphorus, some inert substance to increase the friction (such as ground glass or flint), and glue mixed with some coloring matter. The stick is dipped by a machine into the melted paraffin, which

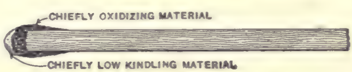


FIG. 76. — CROSS SECTION OF A MATCH.

soaks into the wood. It is next dipped by the same machine into a paste composing the "head," and is then dried. The glue serves to bind the materials together and also protects the phosphorus from the action of the air. On rubbing, sufficient heat is generated to ignite the phosphorus in contact with the oxidizing substance. The heat of this combustion is sufficient to ignite the paraffin, and the burning of this will in turn bring the wood to its kindling temperature.

As friction matches are always a source of fire hazard, they are often prohibited and are replaced by *safety* matches, the heads of which consist of antimony trisulphide, some oxidizing agent, such as potassium chlorate or dichromate, and a little powdered glass to increase the friction, all held together with glue. The box against which they are rubbed has a surface of a thin layer of red phosphorus mixed with antimony trisulphide, manganese dioxide and glue. Sometimes dextrin replaces the glue. As the head of the safety match is soft, it will rub off on a rough surface and not burn, but it will usually ignite on a hard, smooth surface that is a poor conductor of heat, like glass or slate blackboard.

To prevent the smoldering of glowing matches, the sticks are sometimes treated with a fireproofing material, such as a solution of sodium phosphate or alum. The stick is then said to be "impregnated" and is no longer a source of danger when thrown into waste by some careless person.

273. Compounds. — Phosphorus, like nitrogen, forms several oxides and acids. *Phosphoric oxide*, P_2O_5, is formed when phosphorus burns in a sufficient supply of air or oxygen. It is a white solid, which combines energetically with water, forming phosphoric acid, H_3PO_4.

Phosphorus oxide, P_2O_3, forms when phosphorus burns with a limited supply of oxygen. This white solid combines with water, forming phosphorous acid, H_3PO_3.

Phosphoric acid, H_3PO_4, has several salts of common occurrence: ordinary sodium phosphate, Na_2HPO_4, used in medicine; calcium phosphate, $Ca_3(PO_4)_2$, the principal mineral constituent of the bones; monocalcium acid phosphate, $CaH_4(PO_4)_2$, used in baking powder and fertilizers.

ARSENIC

274. Arsenic is generally found in nature combined with sulphur, associated with iron and copper. The ore is roasted, forming arsenious oxide, which is then reduced with carbon:

$$As_2O_3 + 3\,C \longrightarrow 2\,As + 3\,CO$$

275. Properties. — Arsenic is a brittle, steel-gray, crystalline solid, with a metallic luster, and tarnishes rapidly in the air. It volatilizes without melting at the ordinary atmospheric pressure and has an odor like garlic. It burns with a bluish flame, forming the oxide, As_2O_3. In its physical properties, arsenic resembles the metals, but in its actions, it resembles the non-metals, especially phosphorus.

276. Uses. — Arsenic is added to lead in the manufacture of shot. The melted alloy of lead and arsenic is dropped from a height through a strainer or collander into water. The arsenic lowers the melting point of the lead and makes it more fluid, so that the shot becomes spherical before cooling. The arsenic also makes the shot harder than pure lead.

277. Compounds. — *Arsenious oxide*, "white arsenic," As_2O_3, is a crystalline powder, slightly soluble in water,

and, like all compounds of arsenic, is poisonous. It is used in the manufacture of certain colors, also in medicine, and as a poison. *Sulphides of arsenic*, realgar, As_2S_2, and orpiment, As_2S_3, are used as pigments. Paris green is a copper and arsenic compound used as pigment and as insecticide.

ANTIMONY

278. Antimony is found combined with sulphur. It is prepared in a manner analogous to that for arsenic, or by heating the sulphide with iron:

$$Sb_2S_3 + 3\,Fe \longrightarrow 2\,Sb + 3\,FeS$$

279. Properties and Uses. — Antimony is a brilliant, silver-white, crystalline, brittle solid, with a pronounced metallic luster. It does not tarnish in air, but when heated in the air, burns, forming the oxide, Sb_2O_3. As it does not change in air, it is used to cover other materials, such as brass and lead alloys. When finely powdered, it is called *antimony black*, and is used to coat plaster casts in imitation of metal. Antimony alloys are usually hard. Britannia metal and pewter contain copper, tin, lead, and antimony. Babbitt metal and other anti-friction alloys for bearings generally contain antimony.

Lead contracts on solidifying; an alloy of antimony, lead, and tin expands on solidifying, and is hard. This alloy is used for type metal.

BISMUTH

280. Properties and Uses. — Bismuth resembles antimony, but is more metallic. It has a red tinge, is brittle, crystalline, heavy, and tarnishes slowly in moist air.

Bismuth alloys are remarkable for their low melting-points. Bismuth melts at 270° C. Its two most common

alloys, Wood's metal and Rose's metal, have the following composition:

	Wood's Metal	Rose's Metal
Bismuth	50.0 %	48.9 %
Tin	12.5 %	23.6 %
Cadmium	12.5 %	. . .
Lead	25.0 %	27.5 %
Melting points	65° C.	95° C.

Such easily melted alloys are extensively used as fuses in electric connections, in fire alarms, in safety plugs for boilers, and in automatic sprinklers in buildings. When the fusible plug of a sprinkler (Fig. 77, *a*) melts, the water rushes out from the main and strikes a cap *b*, scattering the water in all directions. A piece of Wood's metal is sometimes placed in the gaspipe where it enters the building, so that in case of fire the alloy will melt and stop the flow of gas.

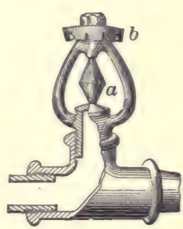


Fig. 77.

281. Comparison of the Nitrogen Group.

	Atomic Weight	Melting Point	Hydrides	Oxides	Acids
Nitrogen	14	$-214°$	NH_3	N_2O, NO, N_2O_3 NO_2, N_2O_5	HNO_2 HNO_3 Strong acids
Phosphorus	31	44°	PH_3	P_2O_3, P_2O_5	H_3PO_3, H_3PO_4 Weak acids
Arsenic	75	volatile . . .	AsH_3	As_2O_3, As_2O_5	H_3AsO_3, H_3AsO_4
Antimony	120	630°	SbH_3	Sb_2O_3, Sb_2O_5	H_3SbO_4 Very weak acids
Bismuth	208	269°		Bi_2O_3	$Bi(OH)_3$, Base

SUMMARY

Phosphorus exists in allotropic forms. The common ones are the white and the red. **White phosphorus** is the more active, is very inflammable and poisonous, and dissolves in carbon disulphide.

Red phosphorus is not so easily ignited, is less active chemically, and does not dissolve in carbon sulphide.

Phosphorus is extracted by the heat developed by passing an electric current through a mixture of rock phosphates, sand, and coke.

Phosphorus is chiefly **used** for making matches and hard alloys.

Arsenic, though a non-metal, shows some of the characteristics of metals. It alloys with other metals and is used to make shot hard. Some of its compounds are valuable as pigments.

Antimony shows the characteristics of both metals and non-metals. It is a constituent of type metal and other alloys.

Bismuth is a metal used in many alloys. These alloys generally have low melting points.

EXERCISES

1. What is the per cent of phosphorus in calcium phosphate of the formula, $Ca_3(PO_4)_2$?

2. Make a sketch of the electric furnace for extracting phosphorus. Label each part. Why must air be kept out?

3. Compare, in tabular form, white and red phosphorus with respect to (*a*) solubility in water and in carbon disulphide, (*b*) melting points, (*c*) ease of ignition, (*d*) chemical activity, (*e*) poisonous nature.

4. What weight of oxygen would be consumed in combining with 0.5 gram of phosphorus? What would be the volume of the oxygen at standard conditions?

5. Why is white phosphorus kept under water?

6. What may be produced during the slow oxidation of white phosphorus?

7. What weight of phosphorus would be necessary to remove the oxygen from 10 liters of air (measured at standard conditions)?

8. How may red phosphorus be changed to white? White to red?

9. Why does white phosphorus cause such bad burns?

10. State the essential differences between a safety and a friction match. How does the safety match justify its name?

11. Write equations to show that both phosphorous oxide and phosphoric oxide are acid anhydrides.

12. Why do matches ignite on being rubbed?

13. What is (*a*) phosphor bronze? (*b*) white arsenic? (*c*) type metal? (*d*) Wood's metal? (*e*) Rose's metal?

14. Describe the operation of an automatic sprinkler.

15. Reduced to standard conditions, 500 c.c. of phosphorus vapor weigh 2.79 grams. From this calculate (*a*) the vapor density, (*b*) the number of atoms in a molecule of gaseous phosphorus.

CHAPTER XXIV

THE HALOGENS

THE elements fluorine, chlorine, bromine, and iodine are called *halogens* (salt formers), because they unite directly with a large number of metallic elements to form salts.

BROMINE

282. Occurrence. — Bromine was discovered in 1826 by Ballard, who separated it from the mother liquor of sea salt, known as *bittern* on account of the bitter taste imparted by magnesium salts. Extensive deposits of magnesium salts containing bromides are found in the almost inexhaustible salt beds at Stassfurt, Germany. The United States and Germany furnish a large percentage of all the bromine used. Large deposits of crude salt, impure sodium chloride, occur in the states of Michigan, West Virginia, Ohio, and Kentucky. Magnesium bromide and sodium bromide are two of the substances mixed with the sodium chloride.

283. Commercial Preparation. — When the brines from these deposits are evaporated, nearly all of the sodium chloride crystallizes out before the magnesium salts begin to separate in an appreciable quantity. The liquid remaining after a portion of the substances contained in the original solution has crystallized, is known by the technical name of *mother liquor.* The mother liquor containing the magnesium chloride is allowed to trickle

down through a tower filled with small pieces of stone or brick. Chlorine gas enters at the bottom of the tower, and, as it rises, reacts with the descending solution:

$$MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$$

High pressure steam introduced into the apparatus causes the liberated bromine and any excess of chlorine to pass over at the top of the tower. The bromine is condensed in a receiver and is afterwards freed from any chlorine by redistillation.

284. Laboratory Preparation. — Bromine can be prepared from the bromides by a method analogous to one of the methods described for the preparation of chlorine; namely, by heating a mixture of a bromide, manganese dioxide, and sulphuric acid (Fig. 78). Bromine, having a low boiling point, passes off in the state of vapor, which can easily be liquefied by keeping the receiver cool. If a small quantity is made, the bromine vapor can be condensed in a test tube partly filled with water (see *a* and *b* in Fig. 78).

FIG. 78. — PREPARATION OF BROMINE.

The reaction may be considered as taking place in three steps.

Sulphuric acid reacts with potassium bromide to produce potassium sulphate and hydrogen bromide:

$$2\,KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HBr$$

When warm sulphuric acid is added to manganese dioxide, manganese sulphate, water, and oxygen are formed:

$$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + O$$

Nascent oxygen oxidizes hydrogen bromide, forming water and bromine:

$$2\,HBr + O \longrightarrow H_2O + Br_2$$

The equation for the complete reaction is:

$$2\,KBr + MnO_2 + 2\,H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 2\,H_2O + Br_2$$

285. Physical Properties. — Bromine is a dark brownish-red liquid, about three times as dense as water. It is the only non-metallic element that exists in the state of a liquid under ordinary conditions. Bromine has an odor somewhat resembling that of chlorine; its name is derived from a Greek word meaning stench.

When a bottle of bromine is opened, the brownish-red vapor of bromine can be seen issuing from its mouth. If a few drops of bromine are poured into a large bottle filled with air, the vapor is seen first at the bottom of the bottle, and from here it diffuses slowly until it fills the bottle.

The vapor of bromine has a strong corrosive action on the mucous membrane. When it comes into contact with the eyes, the irritation is sufficient to cause a copious flow of tears. Great care should be taken not to inhale bromine vapor, and never to allow the bromine to come in contact with the skin. If bromine is accidentally inhaled, the irritation can be lessened by smelling of ammonia, chloroform, or alcohol. If bromine should come in contact with the skin, the injured part should be washed freely with water and then covered with a paste made by mixing sodium bi-

carbonate with water, or better, with some oil, as olive or cocoanut.

Bromine is somewhat soluble in water; the solution is called *bromine water*. Bromine is more soluble in aqueous solutions of the bromides than it is in pure water. It is very soluble in chloroform and in carbon disulphide; in both solutions it has a very characteristic reddish yellow color.

286. Chemical Properties. — The chemical behavior of bromine very closely resembles that of chlorine. Bromine is, however, not so active an element as chlorine. We have already seen that when a mixture of chlorine and hydrogen is placed in the sunlight, the elements combine with explosive violence to form hydrogen chloride. Under similar conditions, bromine vapor and hydrogen enter into only a partial combination, without any *display* of energy. Aqueous solutions of bromine bleach many dyes, but the action is not so rapid as in the case of chlorine.

Bromine combines directly with a number of elements, as phosphorus, antimony, copper, and iron, forming bromides.

287. Uses. — Bromine is used in the preparation of bromides and as a mild oxidizing agent in the manufacture of many organic compounds, especially certain drugs and dyes. Its water solution is used in the laboratory as an oxidizing agent. Bromine is sometimes used as a disinfectant, particularly when conditions might lead to an epidemic.

HYDROBROMIC ACID

288. Preparation. — Hydrogen bromide may be prepared by the direct combination of bromine with hydrogen; the method, however, is of no practical importance.

The addition of sulphuric acid to a bromide would probably appear to be a convenient method for the preparation

of hydrogen bromide. A dilute solution of hydrobromic acid is prepared, on a commercial scale, by the reaction between diluted sulphuric acid and a solution of potassium bromide. The actual carrying-out of the process requires considerable time and careful regulation of temperature.

When concentrated sulphuric acid is added to potassium bromide, hydrogen bromide appears as a gas, which fumes as soon as it comes in contact with the air. Other gases are formed at the same time; the odor of sulphur dioxide can generally be detected, and sometimes that of hydrogen sulphide. The products formed vary with the concentration of the sulphuric acid and the temperature at which the reaction takes place. The more concentrated the sulphuric acid, and the higher the temperature, the less will be the amount of the hydrogen bromide produced.

Let us consider the reactions involved when sulphur dioxide is formed. Sulphuric acid reacts with potassium bromide to form potassium sulphate and hydrogen bromide:

$$2\,KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HBr$$

The excess of concentrated sulphuric acid, however, oxidizes part of the hydrogen bromide, the result of the oxidation being water and bromine:

$$2\,HBr + H_2SO_4 \longrightarrow 2\,H_2O + SO_2 + Br_2$$

This is similar to the action of hot, concentrated sulphuric acid with copper (§ 220), in which a portion of the sulphuric acid is reduced to sulphur dioxide, and at the same time water is formed. The fact that when one substance is oxidized some other substance is reduced, should be constantly kept in mind.

If we use one equation to represent the formation of

bromine and sulphur dioxide, by the method just considered, we obtain:

$$2\,KBr + 2\,H_2SO_4 \longrightarrow K_2SO_4 + 2\,H_2O + SO_2 + Br_2$$

289. Properties and Uses. — Hydrogen bromide is a colorless gas, readily soluble in water, and its solution, *hydrobromic acid*, possesses the characteristic properties of a strong acid. It is easily oxidized by the oxygen of the air, water and bromine resulting from the oxidation.

Dilute solutions of hydrobromic acid are used to some extent for medicine, and the bromides are an important series of salts.

290. Replacement of Bromine. — When chlorine is added to a solution of a bromide, free bromine appears and chlorine molecules change into chlorine ions. The solution of potassium bromide contains potassium ions, bromine ions, and molecules of potassium bromide; the undissociated and dissociated potassium bromide are in equilibrium. As soon as chlorine is added, the bromine ions give their negative charge of electricity to the chlorine molecules, which then dissociate into ions. The bromine ions, having lost their charge of electricity, unite to form bromine molecules. As soon as some of the bromine ions pass out of solution, the equilibrium between the dissociated and the undissociated potassium bromide is destroyed, and more molecules of potassium bromide dissociate. If enough chlorine is added, all the bromine ions will finally appear as bromine molecules, and the solution will contain potassium ions, chlorine ions, molecules of potassium chloride, and molecules of bromine:

$$2\,K^+ + 2\,Br^- + Cl_2 \longrightarrow 2\,K^+ + 2\,Cl^- + Br_2$$

or

$$2\,KBr + Cl_2 \longrightarrow 2\,KCl + Br_2$$

The presence of bromine can be shown by adding a little chloroform or carbon disulphide, and shaking. These liquids and water are not miscible (§ 52), and bromine is much more soluble in carbon disulphide than it is in water. The bromine will be distributed between the water and the carbon disulphide in proportion to its solubility in the two liquids. The solution of bromine in carbon disulphide has a characteristic color; the bromine must be free, for bromine ions do not produce the characteristic color, as is shown by shaking carbon disulphide with a solution of potassium bromide (Fig. 79, *a*). Since a small quantity of carbon disulphide can be used to remove nearly all of the free bromine from a comparatively large quantity of water by shaking, the process is called *shaking out* or *extraction*.

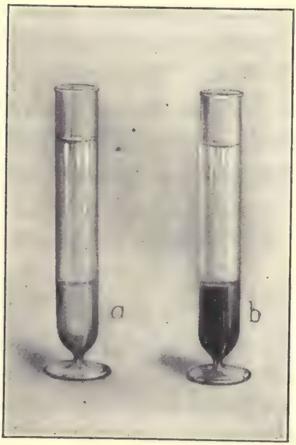


FIG. 79.

291. Test for a Bromide. — The liberation of bromine by chlorine, followed by shaking out with chloroform or carbon disulphide, is used as a test for bromine ions. If we add chlorine water to a solution of a bromide, and then shake with chloroform, the latter dissolves the free bromine, acquiring the characteristic reddish yellow coloration (Fig. 79, *b*). Another test for a bromide depends upon the fact that silver bromide separates as a yellowish white precipitate when a solution of silver nitrate is added to a solution of a bromide. It is insoluble in nitric acid, slightly soluble in dilute ammonium hydroxide, and more readily soluble in concentrated ammonium hydroxide.

IODINE

292. Discovery. — Iodine was discovered by Courtois in 1812 while trying to prepare potassium nitrate from liquors obtained by washing the ashes of burnt seaweed. During his experiments Courtois observed the violet color of the vapor of iodine, but the properties of the element were first carefully studied by Gay-Lussac.

293. Preparation. — When seaweed (kelp) is burned at a low temperature, the ash contains considerable quantities of the iodides of potassium and sodium. As both of these salts are readily soluble in water, they can be separated from the insoluble portion of the ash by *leaching*, that is, by allowing water to pass slowly through the ash and dissolve the soluble materials.

Iodine is obtained from potassium iodide by a process analogous to that described for the preparation of bromine (§ 284); the iodide is warmed with manganese dioxide and sulphuric acid. Iodine passes off in the form of a vapor:

$$2KI + MnO_2 + 2H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 2H_2O + I_2$$

Large deposits of impure sodium nitrate are found in the dry region west of the Andes. Compounds of iodine occur in these deposits, and most of the iodine used is obtained from the mother liquor of the sodium nitrate works.

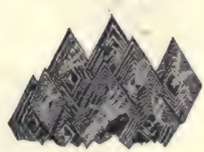


FIG. 80.—IODINE CRYSTALS.

294. Physical Properties. — Iodine is a steel-gray solid (Fig. 80), very slightly soluble in water, but readily soluble in alcohol, chloroform, carbon disulphide, and in aqueous solutions of potassium iodide. A solution of iodine in alcohol is called *tincture of iodine*. Solutions of

iodine in chloroform and in carbon disulphide possess a characteristic violet color; iodine vapor has the same color. Iodine vaporizes slowly at ordinary temperatures. When the solid is warmed, the change takes place rapidly, and the vapor on being cooled passes directly to the state of a solid. Such a distillation of a solid is called *sublimation*, and may be used to purify solids that can be sublimed, as distillation is used to purify liquids.

The fact that iodine is more soluble in a solution of an iodide than in pure water is explained by the supposition that iodine ions combine with the iodine molecules to form triiodine ions:

$$I^- + I_2 \longrightarrow I^-_3$$

The difference between the color of a solution of iodine in chloroform and the color of a solution of iodine in an aqueous solution of an iodide is due probably to the difference in the number of atoms in the particles of iodine entering the solution.

FIG. 81.

295. Chemical Properties. — Iodine unites directly with many elements to form iodides. The reactions are not as energetic as in the case of either chlorine or bromine. When a piece of yellow phosphorus and a piece of iodine are brought together, they combine to form an iodide without the application of heat (Fig. 81). Iodine and iron unite when heated.

When a dilute solution of iodine is mixed with a dilute solution of starch paste, a characteristic blue color is produced. The reaction is employed in testing for either iodine or starch.

296. Uses. — Iodine compounds are used in medicine, in photography, and for dyeing. Tincture of iodine is used for reducing swellings and as a disinfectant for wounds.

297. Preparation of Hydriodic Acid. — If concentrated sulphuric acid is added to an iodide, the odor of hydrogen sulphide is very noticeable. More hydrogen sulphide is produced than is formed when sulphuric acid is added to a bromide. This means that hydriodic acid is more easily oxidized (or is a better reducing agent) than hydrobromic acid.

The formation of iodine by the action of sulphuric acid with potassium iodide can be represented by the following equations:

$$8\,KI + 4\,H_2SO_4 \longrightarrow 4\,K_2SO_4 + 8\,HI$$
$$H_2SO_4 + 8\,HI \longrightarrow H_2S + 4\,H_2O + 8\,I$$

The equation for the complete reaction is:

$$8\,KI + 5\,H_2SO_4 \longrightarrow 4\,K_2SO_4 + 4\,H_2O + H_2S + 8\,I$$

Hydriodic acid can be readily prepared by the reaction of water with iodine and red phosphorus:

$$P + 3\,I \longrightarrow PI_3$$
$$PI_3 + 3\,H_2O \longrightarrow H_3PO_3 + 3\,HI$$

298. Iodides. — The iodides are important compounds, finding extensive use in medicine.

Both chlorine and bromine liberate iodine from the iodides:

$$2\,KI + Cl_2 \longrightarrow 2\,KCl + 2\,I$$
$$2\,KI + 2\,Br \longrightarrow 2\,KBr + 2\,I$$

The presence of free iodine can be determined by the starch test or by shaking out with chloroform or carbon disulphide.

THE HALOGENS AS A GROUP

299. Comparison of the Properties of the three halogens, chlorine, bromine, and iodine, leads to some interesting results:

Name of Element	Atomic Weight	State	Solubility in One Part of Water at 15° C.	Heat of Formation of Hydrogen Comp.	Heat of Formation of Potassium Comp.
Chlorine	35.5	Gas	2.4 vol.	22,000 cal.	104,300 cal.
Bromine	80	Liquid	0.032 pt.	8,400 cal.	95,100 cal.
Iodine	127	Solid	0.00015 pt.	−7,000 cal.	80,100 cal.

Chlorine, bromine, and iodine form a natural group of elements. The difference between the atomic weight of bromine and that of chlorine is nearly the same as the difference between the atomic weights of iodine and bromine. An examination of the table will show that the properties of these elements vary in degree with the atomic weights. Chlorine, bromine, and iodine very closely resemble each other in their chemical behavior. The chemical activity of bromine is less than that of chlorine and greater than that of iodine.

300. Heat of Formation. — When a chemical change occurs without the addition of energy, the substances resulting from the reaction usually contain less energy than the original constituents. Chemical energy has been transformed into some other kind of energy. It is most often liberated in the form of heat.

When elements unite to form chemical compounds, the heat evolved or absorbed is called the *heat of formation* of the compound in question. In measuring the heat of formation of any compound, weights of the substances equal to their molecular weights expressed in grams (gram-molecules) are considered, and the quantity of heat is commonly expressed in calories (§ 48). *The heat of formation is the number of calories of heat absorbed or liberated during the formation of one gram-molecule of a compound from its elements.*

Hydrogen unites with chlorine to form hydrogen chloride. The simplest equation representing the reaction is:

$$H + Cl \longrightarrow HCl$$

This shows that 1 gram of hydrogen unites with 35.5 grams of chlorine to form 36.5 grams of hydrogen chloride. During the combination, 22,000 calories of heat are evolved. The thermal equation for the formation of hydrogen chloride is:

$$H + Cl \longrightarrow HCl + 22{,}000 \text{ calories}$$

The heat of formation of hydrogen chloride is 22,000 calories.

When hydrogen combines with iodine to form hydrogen iodide, an absorption of heat occurs. The thermal equation reads:

$$H + I \longrightarrow HI - 7000 \text{ calories}$$

This shows that when 1 gram of hydrogen unites with 127 grams of iodine, 7000 calories of heat are absorbed. The heat of formation of hydrogen iodide is $-$ 7000 calories.

301. Relative Replacement and Heats of Formation. — Let us use the double arrow in the following equation to indi-

cate the two possible directions in which the reaction *might* proceed:

$$HCl + Br \rightleftarrows HBr + Cl$$

Would bromine actually replace chlorine or would the reverse be true? The following generalization has been developed from the study of the heat effects of many chemical changes.

When a chemical reaction takes place without the addition of heat from an external source, those substances which have the greatest heat of formation will tend to form.

The heat of formation of hydrogen bromide is 8400 calories; that of hydrogen chloride is 22,000 calories. Thus more heat is liberated when hydrogen unites with chlorine than is liberated when hydrogen combines with bromine. We should therefore expect chlorine to liberate bromine from hydrogen bromide. Chlorine *does* liberate bromine from hydrogen bromide. Either chlorine or bromine liberates iodine from hydrogen iodide, as the heats of formation of hydrogen chloride, bromide, and iodide would lead us to expect. A study of the heats of formation of chemical compounds has been of value in the prediction of chemical reactions.

It should be remembered that heat is not the only form of energy into which chemical energy is converted, and in cases of solution in which chemical compounds are dissociated, the energy necessary to dissociate the compounds is an important factor in the thermal equation.

FLUORINE

302. Activity. — Fluorine belongs to the halogen group, but does not so closely resemble the other members of the group as they resemble each other. A consideration of

fluorine has therefore been made to follow a study of the other members of the group.

Fluorine is an element of unusual chemical activity; few substances are not attacked by it. It cannot be isolated in the presence of water, as it unites with the hydrogen in the solution and liberates the oxygen. Furthermore, it cannot be prepared in glass vessels, as it reacts with the glass. The heats of formation of the fluorides are too great to permit of their being easily decomposed by heat. From the statements just made it will be seen that fluorine cannot be prepared by the methods generally employed in the preparation of the other halogens.

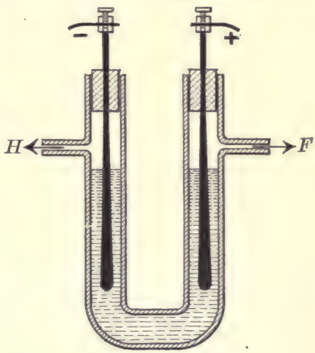


FIG. 82.

303. Preparation. — The problem of isolating pure fluorine puzzled chemists until 1886, when Moissan discovered that a solution of potassium fluoride in liquid hydrofluoric acid conducted the electric current. The apparatus used by Moissan to carry on the electrolysis consisted of a U-tube made of an alloy of platinum and iridium, carrying electrodes composed of the same material, which were insulated from the U-tube by calcium fluoride stoppers (Fig. 82). Moissan subsequently found that a U-tube made of copper could be substituted for the one composed of the expensive alloy mentioned.

The solution of potassium fluoride in hydrofluoric acid was placed in the U-tube and kept at a temperature near − 23° C. during the electrolysis.

Fluorine is liberated at the anode, during the electrolysis,

and passes off through the side arm of the tube surrounding it. Hydrogen is liberated at the cathode. Potassium passes to the cathode, but, on giving up its electric charge, instantly unites with fluorine, forming potassium fluoride, which dissolves in the excess of hydrofluoric acid. The result of this electrolysis is that only the hydrofluoric acid is permanently decomposed.

304. Properties. — At ordinary temperatures, fluorine is a nearly colorless gas, much more poisonous than chlorine. Liquid fluorine combines energetically with hydrogen, sulphur, phosphorus, arsenic, some other elements, and many compounds, showing that violent chemical action can take place at a very low temperature.

Under ordinary conditions, fluorine has a greater tendency to form compounds than any other element. Copper when placed in fluorine becomes coated with an insoluble coating of copper fluoride. The fluorides of calcium, strontium, and barium are insoluble. Silver fluoride is soluble. Gold and platinum, which readily form compounds with nascent chlorine, are very slowly attacked by fluorine. No oxide of fluorine is known. It is interesting to compare the properties of fluorine just mentioned with those of chlorine, bromine, and iodine.

Two compounds of fluorine that occur in nature are of importance: calcium fluoride or fluor spar, CaF_2, and cryolite, $3\,NaF \cdot AlF_3$. Cryolite is used in the preparation of aluminum by the electrolytic process.

305. Hydrofluoric Acid. — Hydrofluoric acid is prepared by the action of sulphuric acid with fluor spar:

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF$$

The reaction is commonly carried on in a lead or platinum dish.

Pure hydrogen fluoride is a colorless liquid which fumes strongly in air. It dissolves readily in water and aqueous solutions of it are sold in wax bottles. Great care should be exercised in using this acid, as painful sores, difficult to heal, are produced when it comes in contact with the skin. There have been cases where the inhalation of hydrogen fluoride vapor has caused death.

The *chief use* of hydrofluoric acid is in the etching of glass. Glass is composed of silicates, and hydrofluoric acid converts the silica (silicon dioxide) of the glass into a gas, silicon fluoride, and water:

$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$

Glass is prepared for etching by covering it with a coating of some substance that is not attacked by hydrofluoric acid, such as paraffin or a mixture of beeswax and rosin, and then removing the coating with a sharp instrument from the part to be etched. The etching is accomplished by subjecting the prepared piece to hydrofluoric acid vapor, or by applying to it a water solution of the acid (Fig. 83). When the gas is used the surface of the etching is left dull, while with a water solution it is left glossy. Hydrofluoric acid is used in the finishing of cut glass, and for the removal of sand from castings. Sodium and ammonium fluoride solutions also are used for etching glass.

FIG. 83. — ETCHING WITH HYDROFLUORIC ACID.

SUMMARY

Bromine, atomic weight, 80, resembles chlorine very closely. The chief points of difference are that it is a dark-colored liquid and that it is less active. In general, bromine reactions resemble those of chlorine, but are of less intensity.

Bromides are found in nature associated with chlorides. Bromine is **prepared** from bromides by a process exactly analogous to that used in the preparation of chlorine from sodium chloride. A mixture of a bromide and manganese dioxide is treated with concentrated sulphuric acid. The manganese dioxide acts as an oxidizing agent on the hydrobromic acid that is formed by the action of the sulphuric acid with the bromide.

Hydrobromic acid is the water solution of hydrogen bromide, which is formed by the action of moderately concentrated sulphuric acid with potassium bromide. There is a marked difference here from the action that occurs in the preparation of hydrochloric acid. The difference is due to the fact that the hydrobromic acid is less stable (*i.e.* has a less heat of formation) than hydrochloric acid. The secondary products formed in the case of hydrobromic acid are mainly sulphur dioxide and free bromine, resulting from the oxidizing action of the sulphuric acid.

Bromine and its compounds are not of great commercial importance. Bromides are **used** in medicine, and free bromine is used in the preparation of certain dyes.

Since bromides have smaller heats of formation than the corresponding chlorides, free **chlorine will displace bromine** from bromides. The presence of free bromine in solution may be detected by the color it imparts to carbon disulphide or chloroform.

Iodine, atomic weight, 127, is found as iodides in small quantities in the ashes of sea plants, and associated with sodium and potassium compounds. It is a dark gray solid with the suggestion of a metallic appearance. In its chemical properties it resembles chlo-

rine and bromine, but it is less active than either. Thus we find that with these three elements, as the atomic weight increases, the activity diminishes, and the elements lose something of their non-metallic character.

Iodine may be prepared by a process analogous to that used in the preparation of chlorine or bromine.

Hydriodic acid results from the action of moderately concentrated sulphuric acid with potassium iodide, but only a small part of the expected quantity is obtained. The heat of formation of hydriodic acid is so low that it is very readily oxidized by the sulphuric acid. Sulphur dioxide, free sulphur, hydrogen sulphide, water, and free iodine may all be formed in this secondary action.

Iodides have a less heat of formation than bromides. Consequently free **bromine will displace iodine** from iodides. Chlorine will do the same thing, even more readily.

Fluorine, atomic weight, 19, is the most intensely active element known. Hydrofluoric acid is a stable compound used in etching glass.

The four **halogens, considered as a group**, may be regarded as the most nearly perfect example of a chemical family. The properties change in a very definite and regular way with the change in atomic weight.

EXERCISES

1. How does relative solubility aid in obtaining bromides from the brines of salt deposits?

2. Why should bromine water be kept in a dark place?

3. Write the equations representing the reactions of bromine with zinc, antimony, and hydrogen. Name the products in each case.

4. Account for the odor of sulphur dioxide sometimes obtained when concentrated sulphuric acid is added to a bromide.

5. Prepare a table of the halogens according to the following form:

a	*b*	*c*	*d*	*e*
Element	Atomic weight	Compounds found in nature (Formulas)	Equations for the preparation of element	Physical properties

f	*g*	*h*	*i*
Chemical properties	Relative replacing power in binary compounds	Equations for the preparation of the hydrogen compound	Stability of the hydrogen compound

6. A solution of sodium bromide is treated with an excess of silver nitrate, and 0.65 gram of silver bromide is precipitated. What weight of sodium bromide was contained in the original solution?

7. Define leaching; sublimation; tincture; heat of formation.

8. How would you recover some iodine that had become mixed with sand?

9. Using the formulas for potassium bromide and potassium iodide, write the three equations which show the relative replacement of bromine, chlorine, and iodine.

10. Why is not sulphuric acid used for the preparation of hydriodic acid?

11. A solution contains potassium chloride and potassium bromide. How would you show the presence of the two halogens?

12. What weight of iodine could be obtained from 150 grams of potassium iodide? How much sulphuric acid would be

needed for the action, assuming that the acid sulphate of potassium is produced?

13. Solutions of hydriodic acid become dark colored on standing. To what substance is the dark color probably due? Explain the action that produces it.

14. What laboratory method is equally good for the preparation of chlorine, bromine, and iodine? Write the equations.

15. How would you prove the presence of an iodide, employing the starch test?

16. State how opaque graduations could be marked on a blank gas measuring tube.

CHAPTER XXV

CARBON

306. Unusual Character. — Carbon, though a non-metal, differs in several important respects from the other elements of its class. It forms almost numberless compounds with hydrogen. These substances are called *hydrocarbons.* Besides these, there are many compounds that are composed of carbon, hydrogen, and oxygen; others are known which in addition contain chlorine, bromine, iodine, nitrogen, sulphur or some other element. There are so many of them that the branch of chemistry which deals with them has a special name, *organic chemistry.* Some of the more important organic compounds are treated in Chapters XXXVIII and XXXIX.

307. Importance of Carbon in Nature. — Every living thing, plant or animal, contains carbon in its tissues in the form of organic compounds. The higher plants always contain a large amount of cellulose, which is composed of carbon, hydrogen, and oxygen. Cotton fiber is the purest form of cellulose known.

The muscular tissue of animals is composed of a class of bodies known as *proteins.* They contain carbon, hydrogen, oxygen, and nitrogen, with a very small quantity of other elements. The *fat* of animals is composed of carbon, hydrogen, and oxygen.

308. Occurrence. — In the uncombined form carbon is found as coal, graphite, and diamond. In addition to its

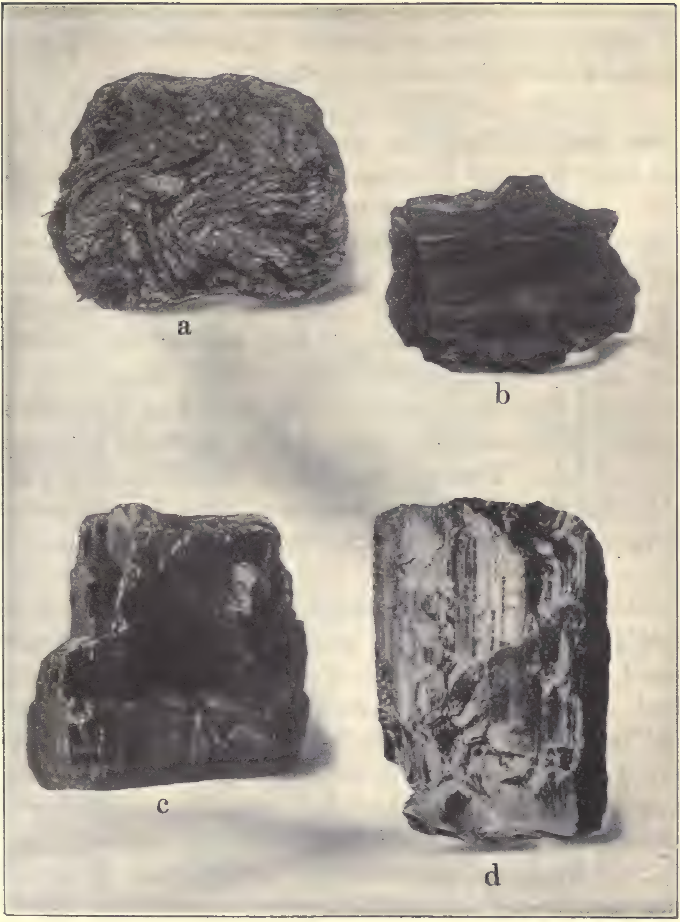


FIG. 84. — FUELS.

a, peat ; *b*, lignite ; *c*, soft coal ; *d*, anthracite.

occurrence in organic compounds, the element is also found in *carbon dioxide* of the atmosphere, and very abundantly in the *carbonates* of certain metals, especially calcium and

magnesium. Marble and limestone are two different varieties of calcium carbonate. A considerable part of the earth's crust is made up of these materials.

309. Coal. — There are two chief forms of coal and several less important varieties. None of them is pure carbon. Anthracite or hard coal (Fig. 84, *d*) contains over 80 % of uncombined carbon. It usually contains a small amount of moisture and a variable quantity of incombustible matter, the ash. Anthracite coal is generally graded in size by screening. The smaller sizes contain more slaty impurities than large sizes. Bituminous or soft coal (Fig. 84, *c*) contains 40 % to 60 % of uncombined carbon. The remaining 60 % to 40 % is chiefly hydrocarbons and ash. The hydrocarbons can be driven off as gases by heating the coal without access of air. This operation furnishes a means of making one kind of illuminating gas.

Coal is fossil vegetable matter. During a part of the earth's history, known in geology as the carboniferous period, vegetation flourished to a remarkable extent. Much of this vegetable matter was buried under beds of mud and sand. In this condition it underwent very slow partial decomposition. A large part of the hydrogen and oxygen was driven off, and the remainder, consisting of uncombined carbon, was left as coal. In anthracite coal the decomposition has proceeded further than in bituminous coal.

Some forms of coal contain even less uncombined carbon than does the bituminous variety. Cannel coal and lignite belong to this class. Lignite exhibits much of the structure of the wood from which it was derived (Fig. 84, *b*). Peat is moss or other loose vegetable matter that, to a slight extent, has undergone a change like that by which

coal was formed (Fig. 84, *a*). Figure 85 shows the composition and heating value of coal, wood, and coke.

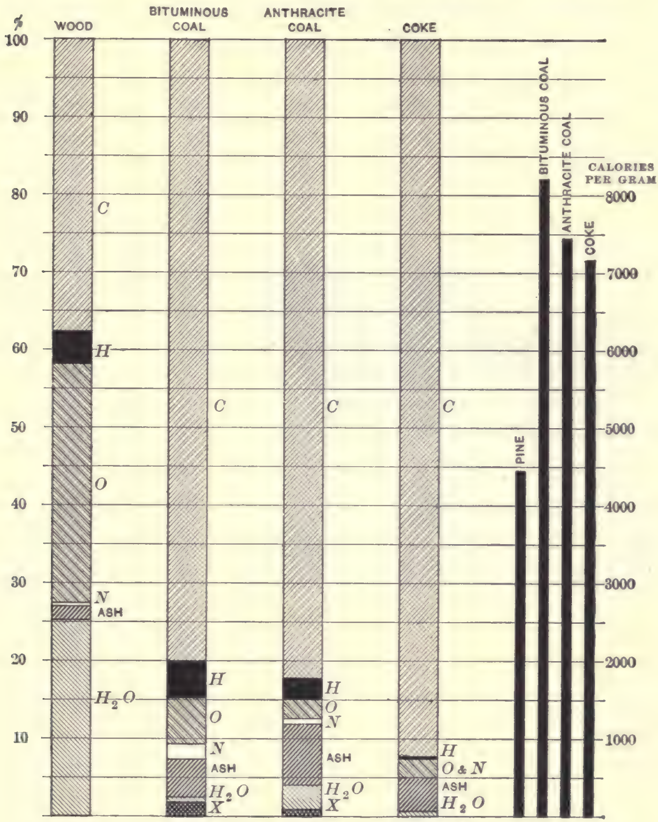


FIG. 85. — COMPOSITION AND HEAT VALUE OF COMMON FUELS.

OTHER COMMERCIAL FORMS OF CARBON

310. Lampblack. — Lampblack, or soot, is practically pure carbon. It is best made by burning hydrocarbon oils with a limited supply of air. The operation is analogous to that which takes place when a kerosene lamp

smokes. The hydrogen of the oil burns, but much of the carbon remains unburned because of the lack of oxygen. The unburned carbon is deposited as a soft, amorphous, slightly greasy powder. Lampblack is used in making paint and printers' ink.

Large quantities of lampblack are made from natural gas by using machines of special design. One of these lampblack machines (Salsburgh patent) is shown in Figure 86. The cast-iron disk (*D*), about four feet in diameter, is mounted on a hollow shaft. The burner (*G*) is mounted close to the disk in such a position that the flames from the tip will be divided, half of the flame depositing a thin coating of soot, or lampblack, on the concave surface, and the other half of the flame depositing a thin coating on the convex surface of the disk.

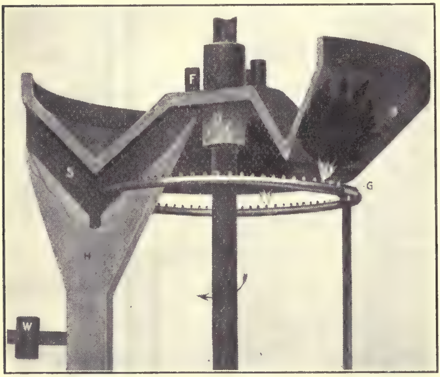


FIG. 86. — MANUFACTURE OF LAMPBLACK.

As the disk revolves slowly in the direction of the arrow, the scraper (*S*) removes the lampblack from the disk and the black powder falls through the hopper (*H*). The lampblack is sifted and prepared for sacking. The top of the disk is kept full of running water, which cools the disk and then empties into the hollow shaft.

311. Wood Charcoal. — Wood charcoal is made by heating wood without access of air. To a certain extent this

operation resembles the natural process by which coal was formed. The hydrogen, oxygen, nitrogen, and some of the carbon which the wood contains pass off in the form of various simpler compounds. The operation is known as *destructive distillation* (Fig. 145, § 504). The charcoal which remains is uncrystallized in form, and retains the cell structure of the wood from which it was formed. Charcoal is not pure carbon, as is shown by the fact that it leaves an ash on burning.

312. Boneblack, or animal charcoal, is obtained by heating bones without access of air. Bones contain both mineral and animal matter. The animal matter, consisting of carbon compounds, is converted into charcoal by destructive distillation; the mineral matter, which is chiefly calcium phosphate, is separated from the charcoal by being dissolved in hydrochloric acid. Boneblack is extensively used for filtering purposes. It has the power of absorbing both coloring matter and gases from solution. This is characteristic of nearly all amorphous substances. Other forms of amorphous carbon have the same property in a less degree. The most important use of boneblack is in the decolorization of sugar and oils.

313. Coke. — Coke is an amorphous form of carbon obtained by the destructive distillation of bituminous coal. It is also obtained as a by-product in the manufacture of one kind of illuminating gas. In the United States nearly 50 million tons of coke are produced yearly and used in the working of metals. The collection of the by-products is an important feature of the operation of the modern coke oven.

Oil coke collects in the retorts used in distilling petroleum. Oil coke is a good and durable conductor of electricity and is used for making carbon rods for arc lights.

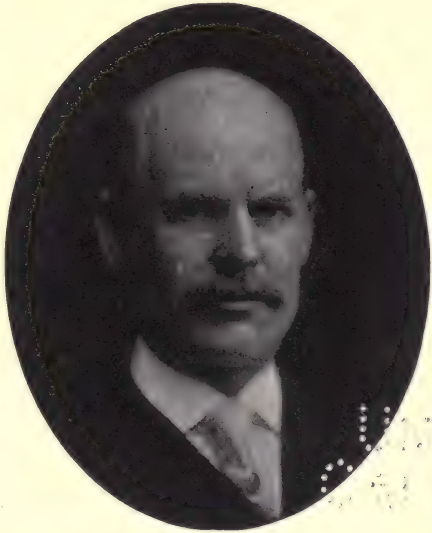
ALLOTROPIC FORMS

314. — Among all the varieties of carbon three distinct allotropic forms are recognized. These are amorphous carbon (of which lampblack is the purest form ordinarily obtained), graphite, and diamond. The different varieties of charcoal, coal, and coke are impure forms of amorphous carbon.

The three allotropic forms can each be burned in oxygen, if raised to a sufficiently high temperature, with the formation of nothing but carbon dioxide. This fact proves that the three substances are different forms of the same element. They differ widely in physical properties and in the ease with which they burn.

315. Amorphous Carbon. — As the name implies, amorphous carbon is without crystalline structure. Its density is low; it is soft, and it does not conduct an electric current very well. These properties cannot be specified definitely because they vary according to the temperature to which the element has been subjected. Amorphous carbon burns with comparative ease.

316. Graphite. — Graphite is a crystalline form of carbon. There are a number of natural deposits of graphite, the best coming from Ceylon, Siberia, and New York. Graphite is now produced artificially by heating anthracite coal in an electric furnace. The crystals of graphite appear as minute scales or plates, which present a very good sliding surface. To this property is due the use of graphite as a lubricant. Artificial graphite may also be prepared in the form of an extremely finely divided powder, which will remain suspended in water or oil (deflocculated graphite). It differs from other forms of



Edward Goodrich Acheson is the inventor of many important processes associated with the graphite and carbon compounds. He is famous chiefly as the discoverer of carborundum, artificial graphite, and deflocculated graphite. In connection with these industries, he has had a great deal to do with the development of electric furnaces. He has invented graphitized anodes, which are much more durable than carbon electrodes in electrolytic furnaces. To meet the need for a highly refractory material he invented siloxicon, a compound of carbon, silicon, and oxygen, which resists fusion even at very high temperatures. He was awarded the Perkin Medal of the Society of Chemical Industry in January, 1910.

carbon in being very soft, in conducting the electric current readily, and in having a very high kindling temperature. Like all forms of carbon, it has a very high melting point. This refractory nature of graphite permits its use in crucibles for melting metals. Its resistance to heat and its conducting power cause it to be extensively used for the melting pots and electrodes of electric furnaces. Graphite is also used for making lead pencils. The varying degrees of hardness in the pencil are secured by mixtures of graphite and clay. Another use of graphite is to prevent the formation of scale in steam boilers.

317. Diamond. — Diamond, the third form, is also a crystallized variety of carbon. It is found as octahedral crystals, sometimes colorless and transparent, sometimes tinted or even black. The diamond differs from the other allotropic forms in being extremely hard. It is the hardest substance found in nature. Like graphite, it burns only when heated to a high temperature. The use of diamonds as gems is due to their great rarity, and to the fact that light in passing through them is highly refracted so that a sparkling play of color results. This effect is heightened by cutting the surface of the stone into numerous facets. The value of a diamond depends largely on its color and its brilliancy. Discolored stones are employed in cutting instruments for use on hard materials.

Microscopic diamonds have been made artificially, but such artificial diamonds have never been obtained clear or of appreciable size.

318. Chemical Properties. — The *physical properties* of carbon have been described in discussing the allotropic forms of the element.

None of the forms of carbon reacts with either acids or bases. They are all insoluble in ordinary solvents. Melted iron dissolves carbon to a certain extent.

Carbon has a great tendency to unite with oxygen at moderately high temperatures. It not only burns in oxygen, but it also unites with the oxygen that is held in combination with other elements. On this account, carbon makes an excellent reducing agent. The reaction of carbon with copper oxide illustrates this property. When the mixture is heated in a hard glass test tube (Fig. 87, *a*) and the gas is led into limewater (Fig. 87, *b*), a white precipitate of calcium carbonate indicates the presence of carbon dioxide, and metallic copper is produced:

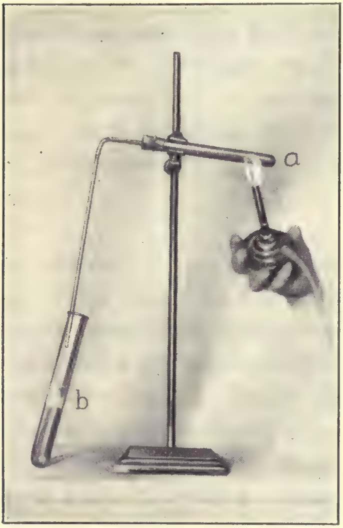


Fig. 87.

$$2\,CuO + C \longrightarrow 2\,Cu + CO_2$$

Enormous quantities of coke are used in the reduction of metals, particularly iron, from their ores.

319. Reactions at High Temperatures. — In spite of the fact that carbon forms so many different compounds with hydrogen, it unites directly with this element only at the temperature of an electric arc, and then very slowly. By using the high temperature of an electric furnace, carbon can be made to unite with many metals and some non-metals.

The intense heat of an electric furnace makes carbon react with lime (calcium oxide), and calcium carbide is formed:

$$CaO + 3\,C \longrightarrow CaC_2 + CO$$

Calcium carbide is used to prepare *acetylene*, a gas which makes an excellent illuminant. The gas is generated by the action of calcium carbide with water at ordinary temperatures:

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

Acetylene is used in bicycle and automobile lamps and in places where the gas supply of a city system is not available.

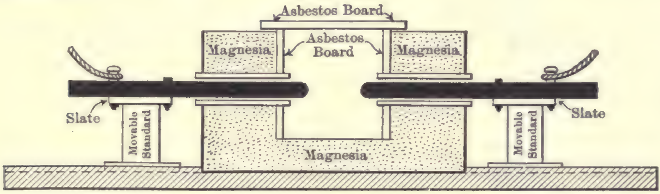


FIG. 88. — LABORATORY ELECTRIC FURNACE.

The electric arc furnace is a device by which a very high temperature is obtained by using a large arc between carbon terminals. The arc consists of carbon vapor, which conducts the current over the gap between the carbons, and the resistance is so great that much heat is developed. A temperature of about 3000° C. is obtained. The reactions that occur in the electric furnace are due to the high temperature. The electric current does not directly play any part in the reactions. A simple laboratory form of furnace is shown in Figure 88.

Carborundum (§ 343), silicon carbide, used as an abrasive, is made by heating sand (silicon dioxide) and carbon in an electric resistance furnace (Fig. 104):

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO$$

When carbon is similarly heated in sulphur vapor, the two elements combine to form carbon disulphide:

$$C + 2\,S \longrightarrow CS_2$$

Carbon disulphide is a heavy, inflammable liquid, with a sweetish odor, when pure, and is valuable as a solvent.

320. Uses of Carbon. — The uses of carbon have been pointed out in the discussion of the properties of the various forms of the element. Coal is the principal source of artificial heat. Anthracite is, in general, the most desirable kind of coal, because it burns with practically no flame and without the formation of soot. It burns more slowly and gives a more uniform heat than does bituminous coal. The use of anthracite is relatively small; about 75,000,000 tons are used annually, and its use is confined to a few localities.

There is over seven times as much bituminous coal produced as anthracite; it is much cheaper, and, weight for weight, produces more heat. Coke burns like anthracite coal and is sometimes used in its place. In warm countries charcoal is often the only fuel used. Many metals are separated from their ores by the aid of coke as the reducing agent. Iron is obtained in this way, usually by the reduction of hematite, ferric oxide. The making of coke from bituminous coal for this purpose is an important industry. Charcoal and boneblack are both used to remove gases and coloring matter from solutions. Impure water is sometimes passed through charcoal filters for purification. This method, while it may suffice for the removal of impurities which can be seen or smelled, is not to be relied upon for the removal of disease germs.

321. Flame of Candle. — We have seen numerous cases of combustion or burning. When the fuel is a solid, par-

ticles of the fuel or of the ash are often heated to incandescence and glow. When a stream of gas burns, a flame is produced. This phenomenon can best be studied in the flame of a common candle.

When a light is applied to the tip of a candle wick, a flame appears and slowly spreads down the wick toward the candle and upward about twice the height of the exposed wick. In a few moments the flame becomes constant in size and position (Fig. 89). Starting about one eighth of an inch from the candle, the flame begins to be visible, rounded at the base and tapering to a sharp point above. It entirely incloses the wick except at the base and at the extreme tip.

FIG. 89.

If we examine the flame closely, we see four parts. The first is a *greenish blue portion of the base*, shaped much like the cup of an acorn. This follows the wick downward a short distance, and its upward extension is hidden by the glare of light within. Second, above and within the first green portion we find, immediately surrounding the wick, a region dark, compared with the more brilliant part above, but in reality transparent and colorless, as is shown by placing an object behind it. This region tapers to a point above and is termed the *non-luminous cone*. Covering the cone just mentioned is a bright cap known as the *luminous cone*. This is the third and most conspicuous region of the flame. Outside the luminous cone we can find the fourth region, which is the faint and scarcely visible blue *mantle*.

The candle is composed of a mixture of paraffin and

stearic acid, both of which contain carbon and hydrogen. The upper portion of the candle, heated by the flame above, melts, so that the top becomes a cup holding a small portion of the melted fuel. This melted portion is drawn up the wick by capillarity, and vaporizing, forms the non-luminous cone immediately surrounding the wick. If we insert a tube into this portion of the flame, we can lead out a quantity of vapor which condenses to a solid similar to that composing the candle. If we extend a thin piece of wire across the flame, we find that it is not very warm near the wick; in fact, the head of a match can be placed there without igniting. There is no combustion in this non-luminous cone since there is no air.

As the vapor is carried upward by the draft it becomes mixed with air and combustion ensues. This region of active burning is brilliant and hot, but not transparent. If we place a piece of cold porcelain in this portion of the flame, or lead off some of the materials through a tube, we find a considerable portion of lampblack (carbon) and moisture. The carbon while in the luminous cone is heated to incandescence.

Since the combustible vapors are slowly mixed with air, the materials may move considerable distances from the wick before they meet sufficient oxygen to burn; hence when a large wick is used, the bulk of vapor makes an extensive region of flame. Indeed, the upper extremity is often so far removed that its temperature falls below the kindling temperature of the combustible materials. These escape unburned and the flame smokes.

In the outer portion of the flame the conditions are reversed, in that the air is in excess. Here the combustion is complete, but usually only a small amount of combustible material reaches this pale outer portion. This material, if drawn out by a tube, is found to be principally air

mixed with products of combustion. The pale green cup below is similarly constituted; but because of its position *below* the principal region of combustion and its nearness to the cool wick and candle, it is not so warm as the blue mantle above.

The wick is made of cotton and is proportioned to the quantity of material to be burned. The cool stream of liquid drawn up the wick protects it from burning, and, at the same time, prevents the flame extending down to the candle. As the candle material is vaporized, the wick chars somewhat but does not burn, since there is no oxygen in its immediate vicinity. In braiding the wick, one of the threads is drawn tighter than the others, so that the wick, when free from the candle-stuff, is drawn over to one side of the flame. This braiding of the wick brings the tip into the outer zone of combustion, where it burns so far as air is available, rotating as the candle shortens and practically maintaining a uniform length. This is why modern candles do not need to be trimmed.

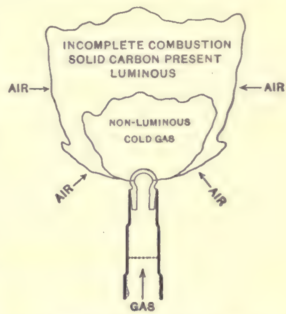


FIG. 90. — FISHTAIL FLAME.

322. Gas Flames. — In the ordinary gas flame (Fig. 90), as well as in the candle flame, the four regions are clearly marked: the region of fuel, or non-luminous cone; the luminous cone, or region of luminosity; outside and lower regions of combustion with an excess of air. The size and shape of gas flames depend largely on the *tip* of the burner. In a Bunsen burner (§ 29) we can adjust the proportions of gas and air so that there shall be no excess of either. Then the flame will appear to have two regions, a lower

cone where no combustion is apparent and the cap above.

In the ordinary flame, we find the position of maximum temperature somewhat above and outside the light-giving materials. A very large part of the energy passes off as heat and only a very small per cent is converted into light. If the solids giving light could be placed above or in the region of maximum temperature, they would evidently be hotter and give more light. Auer von Welsbach accomplished this by placing a mantle composed of a net of infusible and incombustible materials in the outer portion of the flame of a Bunsen burner. The materials are heated to incandescence and produce the brilliant light given by the Welsbach burner.

SUMMARY

Carbon is a non-metallic element, characterized by the **enormous number of compounds** it forms with the non-metallic elements, especially hydrogen, oxygen, and nitrogen.

Carbon is an **inert element at ordinary temperatures**; at higher temperatures it combines readily with oxygen and with a few other elements; at the temperature of the electric furnace it reacts with lime, forming calcium carbide.

Amorphous carbon, graphite, and diamond are the three **allotropic forms of carbon.** These allotropic forms differ widely in physical properties, but all yield the same product when burned in sufficient oxygen.

Carbon is found combined in the tissues of every living thing, in the carbon dioxide of the atmosphere, and in metallic carbonates. Uncombined, it occurs as coal, graphite, and diamond.

Anthracite **coal** is nearly all carbon; bituminous coal is about two thirds carbon and one third hydrocarbons; cannel coal and lignite are poor in uncombined carbon.

The **uses of** the forms of **carbon** are:

Coal: fuel and manufacture of illuminating gas;

Lampblack: paint and printers' ink;

Wood charcoal: fuel and filtering;

Boneblack: filtering and decolorizing sugar and oils;

Coke: fuel, ore reducer, and manufacture of water gas;

Graphite: lead pencils, lubricant, crucibles, and electrodes for high temperatures;

Diamond: gem and abrasive.

The four portions of a **candle flame** are the greenish blue region at the base, the non-luminous cone, the luminous cone, and the blue mantle. The ordinary gas flame has four similar portions, while that of the Bunsen burner appears to have but two — the lower cone and the surrounding conical cap above.

EXERCISES

1. Tell how the carbon in your muscular tissue is indirectly derived from the air.

2. How does anthracite coal differ from bituminous coal in appearance and in chemical composition?

3. Why does soft coal make such a smoky fire?

4. Why is anthracite coal preferred for household use?

5. Explain why fence posts are sometimes charred at the end before being placed in the ground.

6. What properties of lampblack make it suitable for printers' ink and for paint?

7. What kind of carbon is used in batteries?

8. State briefly how you could distinguish between pulverized charcoal and manganese dioxide.

9. What three conditions are necessary for ordinary burning?

10. Why does water put out a fire?

11. Why is a candle extinguished by blowing?

12. In working with compressed air it is found that combustible materials burn more readily than usual. Explain.

13. How many liters of oxygen are required for the complete combustion of 10 liters of acetylene gas? How many liters of air are required?

14. Indicate by a diagram the principal parts of a candle flame. Compare these parts with respect to temperature and light-producing properties. Why is a flame extinguished by surrounding it with carbon dioxide?

15. Why is the flame of a Bunsen burner hotter with the holes open than when they are closed? Is the total heat increased?

16. Why does not the flame of a Bunsen burner extend down the tube to the base?

17. If a taper is held over a gas burner, a flame may be maintained several inches above the burner without "striking back" to the burner. Explain.

18. Describe the structure and the operation of a Welsbach light.

CHAPTER XXVI

OXIDES OF CARBON

CARBON DIOXIDE

323. Occurrence. — There are three very important sources of carbon dioxide: the decay of vegetable and animal matter; the oxidation constantly going on in animals, and to a much smaller extent in plants; the combustion of all ordinary fuels, such as wood, coal, and gas. These fuels consist largely of carbon; this, on burning, combines with oxygen, forming carbon dioxide:

$$C + O_2 \longrightarrow CO_2$$

Hence the gas is always present in the air, usually to the amount of four parts in ten thousand (§ 231). This percentage would be much higher were it not for the fact that plants are constantly taking in carbon dioxide, building the carbon into their tissues, and returning the oxygen to the air.

Natural waters also very commonly contain carbon dioxide; in some spring waters the gas is dissolved in such quantities that they are effervescent, that is, they give off gas in bubbles unless kept in tightly closed vessels. Carbon dioxide is also given off by volcanoes and from other subterranean sources, and from fermenting liquids. It is sometimes found in coal mines, where it is known as *choke damp*.

324. Preparation. — Carbon dioxide is most conveniently prepared in a pure state by the action of a carbonate

with an acid (Fig. 91). Calcium carbonate, which occurs abundantly in the forms of *limestone*, *marble*, and *chalk*, is used on account of its cheapness; and, on a manufacturing scale, sulphuric is the acid selected. But this is not convenient when the carbon dioxide is needed in small quantities, as in the laboratory, because the calcium sulphate which is formed in the action is insoluble and remains as a coating on the pieces of carbonate, thus hindering the action. Hydrochloric acid gives good results because calcium chloride is quickly soluble in water. The equation representing the action is:

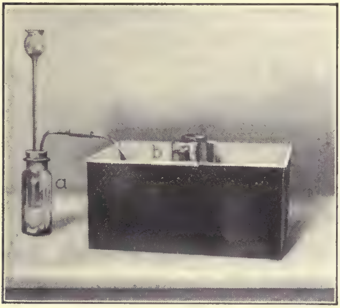


Fig. 91. — Preparation of Carbon Dioxide.

a, generator; *b*, collecting bottle.

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

To remove any hydrochloric acid that may be carried over the gas is allowed to bubble through water. The gas is collected by downward displacement of air or over water.

325. Physical Properties. — Carbon dioxide is a colorless gas with little taste or odor. It is about one and one half times as dense as air, so that it can be poured from one vessel to another like water. Carbon dioxide is sometimes given off from soil and water; and in wells, caves, and mines it frequently collects, because the lack of air movement permits the relatively heavy gas to settle and accumulate.

The gas is soluble in water, which dissolves its own volume at ordinary temperatures. Under increased pres-

sure, water dissolves a greater weight of the gas; if the pressure is removed, the gas is slowly given off, since the weight of a gas which a given volume of a liquid will dissolve is directly proportional to the pressure. An illustration of this property is found in effervescent beverages, which always contain dissolved carbon dioxide.

Carbon dioxide can be liquefied by pressure at ordinary temperatures and the liquid is sold in steel cylinders.

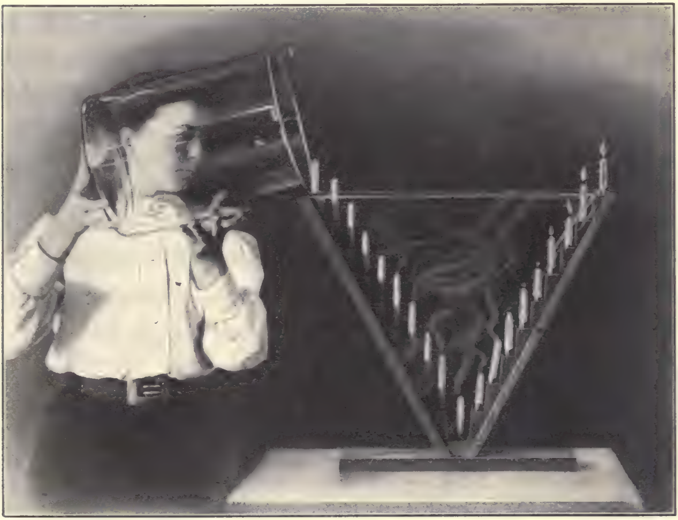


FIG. 92. — CANDLES SUCCESSIVELY EXTINGUISHED BY POURING CARBON DIOXIDE INTO V-SHAPED TROUGH.

326. Chemical Properties. — Carbon dioxide is chemically inactive toward most substances. It is the product of the complete oxidation of carbon, an action which occurs with the liberation of a great amount of energy. Carbon dioxide can, however, be reduced by very active reducing agents, such as burning potassium, sodium, or magnesium. These elements unite with oxygen and set carbon free.

Carbon dioxide does not support combustion (Fig. 92). This property makes it very valuable for use in extinguishing fires.

327. Carbon Dioxide in Air. — Under certain conditions the amount of carbon dioxide in the air may go much above the normal. This does not interfere with either combustion or the process of breathing, unless the increase in carbon dioxide in the air is accompanied by a corresponding decrease in oxygen, which may or may not be the case. The per cent of carbon dioxide in the air is, therefore, not a measure of its fitness for breathing, except as an index to ventilation.

From the standpoint of its relation to life, the most important reaction of carbon dioxide is one that occurs in the leaves of plants, whereby it acts with water under the influence of light and chlorophyl, forming starch and setting free oxygen:

$$6\,CO_2 + 5\,H_2O \longrightarrow 6\,O_2 + C_6H_{10}O_5$$

The water in this reaction comes from the roots of the plant, and the carbon dioxide is taken from the air.

328. Carbonic Acid. — The solution of carbon dioxide has a slightly acid reaction and forms carbonates with bases. Carbonic acid is extremely unstable, and, like ammonium hydroxide, has never been isolated, but the formation of carbonates indicates the presence of hydrogen ions and CO_3^{--} ions. We may write the equation:

$$H_2O + CO_2 \leftrightarrows H_2CO_3$$
$$H_2CO_3 \rightleftarrows H^+ + H^+ + CO_3^{--}$$

Carbon dioxide passed into a solution of a base produces the corresponding carbonate. As calcium car-

bonate is insoluble, calcium hydroxide (limewater) is used as a test for the presence of carbon dioxide. When carbon dioxide is first passed into limewater, it becomes milky, and on standing the precipitate of calcium carbonate settles:

$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,H_2O$$

If the passage of carbon dioxide is continued, the precipitate dissolves. This is because it has been converted into calcium bicarbonate, which is soluble in water:

$$H_2CO_3 + CaCO_3 \longrightarrow CaH_2(CO_3)_2$$

329. Hard Waters. — The solubility of calcium carbonate in water containing an excess of carbon dioxide explains the formation of the kind of *hard water* that is found in regions where limestone is abundant. The surface water, becoming charged with carbon dioxide from decay going on in the soil, dissolves some of the limestone, converting it into calcium bicarbonate. If an attempt is made to use soap with such water, it is found difficult to obtain a lather, as the calcium ions react with the soap to form an *insoluble* soap. By boiling hard water of this kind, part of the carbon dioxide is driven off and the calcium bicarbonate is converted into calcium carbonate:

$$CaH_2(CO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

The carbon dioxide escapes and the calcium carbonate is precipitated. If the rocks contain magnesium carbonate, this may be converted into the bicarbonate and dissolved in the same way as with the calcium compound, and the water may be softened by the same means. Water containing such dissolved bicarbonates is called water of *temporary* hardness. Water of *permanent* hardness generally contains *sulphates* of calcium and magnesium and cannot be softened by boiling.

330. Uses of Carbon Dioxide. — As an easily soluble, non-poisonous gas, carbon dioxide is extensively employed in the manufacture of effervescent beverages. Soda water is water into which carbon dioxide has been forced under pressure (60 to 150 lbs.), and effervesces when drawn. Liquids bottled during fermentation, as champagne and kumiss, effervesce for a similar reason. Seltzer, vichy, and other mineral waters are produced artificially by charging solutions whose composition is similar to that of the original spring.

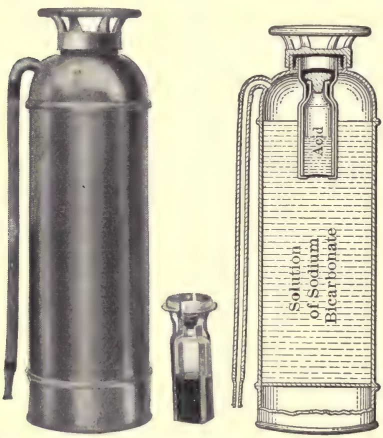


FIG. 93. — FIRE EXTINGUISHER.

One type of *fire extinguishers* (Fig. 93) contains a device for generating carbon dioxide rapidly, as by mixing sulphuric acid with a solution of sodium carbonate when the apparatus is inverted. The pressure of the gas forces a stream of water that contains bubbles of carbon dioxide on the fire. In some chemical engines the pressure of carbon dioxide is sometimes used to throw a stream of water.

The raising of bread and most other forms of *leavening* generally depend on the expansion of bubbles of carbon dioxide by heat. The carbon dioxide is generated by yeast or by the reaction of sodium bicarbonate (baking soda) and a material of acid reaction; for example, acid potassium tartrate, $HKC_4H_4O_6$ (cream of tartar):

$$NaHCO_3 + HKC_4H_4O_6 \longrightarrow NaKC_4H_4O_6 + H_2O + CO_2$$

The compound, sodium potassium tartrate, $NaKC_4H_4O_6$, is known as Rochelle salts.

Liquefied carbon dioxide is used at soda fountains to make soda water. It is also used like ammonia in refrigerating processes, particularly on ocean vessels where the escape of ammonia would be dangerous.

CARBON MONOXIDE

331. Preparation. — Carbon monoxide differs from carbon dioxide in containing one atom of oxygen instead of two. It can be prepared by the reduction of carbon dioxide. This can be accomplished by passing a current of carbon dioxide over carbon heated to redness in an iron tube. The carbon acts as a reducing agent:

$$CO_2 + C \longrightarrow 2\,CO$$

This action takes place in a coal fire. The carbon dioxide, formed near the bottom, is reduced by the hot coal above to carbon monoxide, which is often seen burning at the top of the fire (Fig. 94).

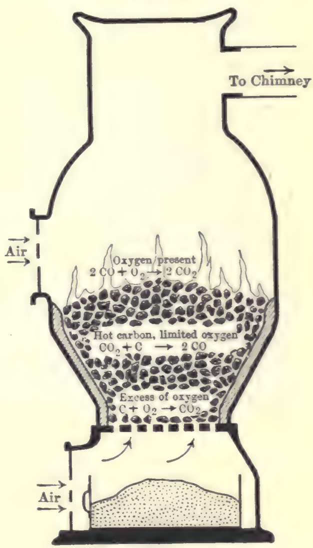


FIG. 94. — CHEMICAL ACTION IN A COAL STOVE.

In the laboratory, carbon monoxide is best made by the decomposition of formic acid (Fig. 95). Warm sulphuric acid is slowly dropped into formic acid. The sulphuric acid, by its dehydrating power, induces an action as follows:

$$HCHO_2 \longrightarrow CO + H_2O$$

The water is absorbed by the sulphuric acid. Oxalic acid gives carbon dioxide by a similar decomposition when treated with sulphuric acid:

$$H_2C_2O_4 \longrightarrow CO + CO_2 + H_2O$$

In this case it is necessary to remove the carbon dioxide from the mixed gases by passing them through a concentrated solution of potassium hydroxide.

FIG. 95. — PREPARATION OF CARBON MONOXIDE.

a, beaker for warming sulphuric acid; *b*, dropping funnel; *c*, flask containing formic acid; *d*, collecting bottle.

332. Physical Properties. — Carbon monoxide is a colorless, odorless gas. It is slightly lighter than air and is nearly insoluble in water. It is extremely poisonous; a very small percentage in the air causes headache, and a larger amount may cause death.

333. Chemical Properties. — Under ordinary conditions the monoxide burns in air with a blue flame. If both the

carbon monoxide and the air are absolutely dry, however, combustion does not take place. Carbon monoxide acts as a powerful reducing agent. The reduction of iron oxide in a blast furnace is largely due to it.

334. Physiological Properties. — Carbon monoxide prevents the oxygen of the air from uniting with the hæmoglobin of the red blood corpuscles, by entering itself into combination with the hæmoglobin to form a stable compound. It is because of this action that a comparatively small amount of the gas will cause death. The compound formed in the corpuscles has a brilliant red color, and is so stable that it can be detected in a body years after death. Carbon monoxide is an important poison in illuminating gas and the gas escaping from stoves. Fortunately in these cases it is associated with compounds having pronounced odors. In spite of this fact, sickness and death are frequently caused by carbon monoxide poisoning.

335. Water Gas. — In addition to its use as a means of reducing metallic oxides, carbon monoxide is commercially important as a constituent of the variety of illuminating gas known as *water gas*. This is produced by the reduction of steam by heated carbon:

$$C + H_2O \longrightarrow H_2 + CO$$

As this mixture of carbon monoxide and hydrogen burns with a non-luminous flame, the gas must be enriched by an addition of gaseous hydrocarbons obtained from petroleum if the gas is to be used for lighting.

Figure 96 shows a generator in which the two operations are combined. Coal in the lower chamber is burned to incandescence by a blast of air. At first, the hot gases pass up through the side pipe and out at *C*. But after

combustion is well under way they are led down through the *carburetor*, and up through the *superheater* and out at C'. The brick checkerwork which these two chambers contain is thus heated to the desired temperature. When this is reached, the first part of the operation, called the *blow*, is terminated. It lasts about 5 minutes.

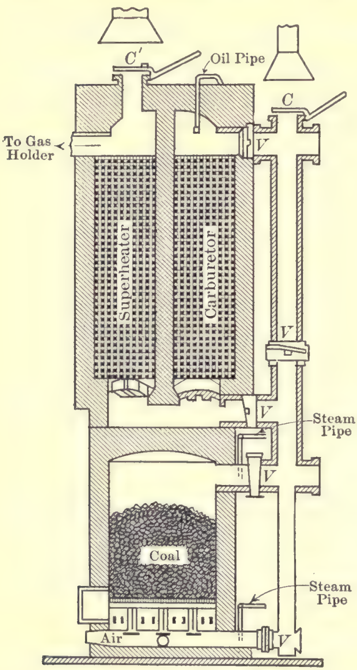


FIG. 96.—WATER GAS GENERATOR.

Then steam instead of air is blown through the incandescent coal, and carbon monoxide and hydrogen are formed. Oil is sprayed into the carburetor, and is decomposed by the heat into gases of high illuminating power that mix with the unenriched gas. The decomposition of the oil vapor is continued and the mixture made uniform in the superheater. The enriched gas passes out the side pipe at the top of the superheater. This second operation, known as the *run*, also lasts about 5 minutes and alternates with the blast.

The various valves (V) shown in the diagram control the passage of the gases so that the temperature in any part of the generator can be perfectly regulated.

336. Producer gas, containing carbon monoxide as its essential constituent, is an important cheap industrial fuel.

It is made by forcing a carefully regulated supply of air through incandescent coal:

$$2\,C + O_2 \longrightarrow 2\,CO$$

The gas contains, in addition to carbon monoxide, a large amount (63%) of nitrogen and a small amount of hydrocarbons obtained from the coal.

The generator, shown in Figure 97, resembles an ordinary stove in construction and operation. Carbon dioxide, formed at the bottom, is reduced to the monoxide while passing through the hot upper layers of coal. In some cases, about 6% of steam is blown in with the air, and a product is obtained which contains a small amount of hydrogen.

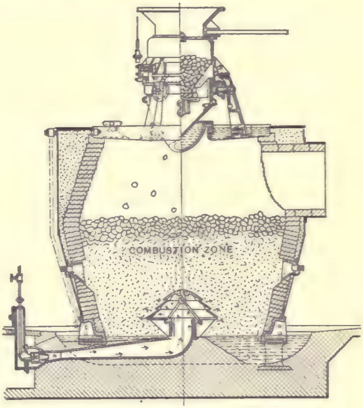


FIG. 97. — GAS PRODUCER.

Producer gas is often obtained as a by-product from blast and other furnaces, and its use is a considerable factor in the economy of the plant.

SUMMARY

Carbon dioxide is formed in the vital processes of plants and animals, and in ordinary combustion.

It is prepared commercially by the reaction of acids with carbonates.

Carbon dioxide is colorless, slightly soluble in water, and suffocating, but not poisonous.

One liter (standard conditions) weighs 1.98 grams.

It reacts with soluble bases, forming carbonates. Small quantities render limewater turbid; excess of the dioxide causes the precipitate to dissolve. Such a solution is **temporary hard water**; boiling expels the excess of carbon dioxide, and the calcium carbonate again separates.

Carbon dioxide is used in charging beverages, in fire extinguishers, and in ice machines.

Carbon monoxide is formed by:

(1) the incomplete combustion of carbon;

(2) the reduction of the dioxide;

(3) the reaction of steam and red-hot coal.

Carbon monoxide is lighter than air, and is very poisonous. One liter (standard conditions) weighs 1.26 grams.

It burns with a pale blue flame, forming the dioxide.

Water gas, used as an illuminant, is obtained by (1) the action of steam on incandescent coal, and (2) enriched by the addition of gases derived from petroleum. Action (1) gives carbon monoxide and hydrogen; action (2) hydrocarbons of high illuminating power.

Producer gas, used only as a fuel, is made by the action of air, sometimes mixed with a small amount of steam, on incandescent coal. Its active constituents are carbon monoxide and small amounts of hydrogen and hydrocarbons. A large amount of inert nitrogen remains in the gas.

EXERCISES

1. How can it be shown that there is carbon dioxide in the air?

2. Give three ways in which carbon dioxide is produced in nature. How is it commonly made in the laboratory? Write

the equation. Write an equation illustrating the use of the same process but with different materials.

3. Why is hydrochloric acid preferred to sulphuric acid in preparing carbon dioxide from calcium carbonate?

4. Why does soda water effervesce when taken from the tank?

5. Describe three important uses of carbon dioxide, and state the properties on which each use depends.

6. Explain how a fire extinguisher puts out a fire.

7. Describe the natural formation of hard water. State how it may be softened. How does hard water differ from distilled water in its action on a soap solution?

8. Why is rainwater preferred for washing purposes in limestone regions?

9. How could you prove that there is carbon in alcohol?

10. By what process may carbon monoxide be obtained from carbon dioxide? Account for the explosions that frequently occur in coal stoves shortly after coal is added. State how these explosions may be avoided.

11. How could you distinguish carbon dioxide from the monoxide?

12. Write the equation for the reaction you would expect if carbon monoxide were passed over hot copper oxide.

13. How would you determine whether a gas was hydrogen or carbon monoxide?

14. Why is it that such a large percentage of the cases of asphyxiation from water gas result fatally?

15. Explain why cases of asphyxiation occur after coal stoves have been filled and left for the night.

16. Calculate the weight of steam that could be decomposed by a ton of incandescent coke containing 90 % carbon.

17. How many grams of calcium nitrate can be obtained by adding sufficient nitric acid to 15 grams of pure calcium carbonate?

18. (*a*) What weight of carbon dioxide is required to precipitate completely as calcium carbonate the calcium in 1 gram of calcium hydroxide?

(*b*) What volume will this weight of carbon dioxide occupy at room temperature and 760 mm.? (One liter of CO_2 at room temperature and 760 mm. weighs 1.90 grams.)

(*c*) Assuming that each bubble of carbon dioxide contains 0.3 c.c., how many bubbles will be required; and assuming that they pass at the rate of 5 per second, how long will the operation take?

19. How many grams of sulphuric acid (H_2SO_4) reacting with an excess of sodium carbonate (Na_2CO_3) are required to produce 200 grams of carbon dioxide (CO_2)?

20. Calculate how many liters of carbon dioxide, at standard conditions, can be obtained by treating 45 grams of pure marble with acid.

21. It has been calculated that an average man exhales 464.5 liters (standard conditions) of carbon dioxide in a day. Calculate how many grams of starch a plant could make from this.

22. Carbon monoxide passed over warm calcium hydroxide reacts:

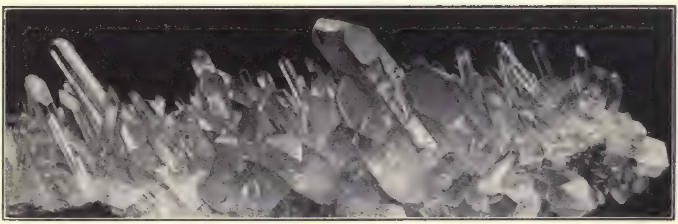
$$CO + Ca(OH)_2 \longrightarrow H_2 + CaCO_3$$

How does the volume of carbon monoxide compare with that of the hydrogen?

CHAPTER XXVII

SILICON AND BORON

337. Silicon. — Silicon, next to oxygen, is the most abundant element in the earth's crust. Nearly all the common rocks are silicon compounds. Silicon, as an element, is of little practical importance. Like carbon, it exists in allotropic forms. It is prepared by reducing silica with aluminum. A small percentage of silicon is found in cast iron and traces of it in steel. It is used as a detector in wireless telegraphy.



Courtesy of the *Brooklyn Museum.*

FIG. 98. — MASS OF QUARTZ CRYSTALS.

338. Varieties of Silicon Dioxide. — Silicon dioxide, or *silica*, SiO_2, is the most common compound of silicon. It is found in many varieties, which differ in color and structure owing to minute quantities of impurities, and to conditions under which they are formed. Quartz, the most common form, crystallizes in hexagonal prisms, surmounted by a pyramid (Figs. 27 and 98). Clear crystalline varieties are known as rock crystal; purple varieties as amethyst. Rose quartz, milky quartz, and smoky

quartz, or cairngorm stone, are other colored varieties of silicon dioxide, which, indeed, is found in all shades and tints, on account of the presence of minute quantities of impurities. Chalcedony is cryptocrystalline and waxlike. Onyx and agate are varieties of chalcedony. Jasper and flint are other forms of silica. Opal is a hydrated form.

The shells of diatoms and many other microscopic organisms are siliceous, and deposits of these comprise the infusorial or diatomaceous earth (Fig. 99). Sand is water-worn silicon dioxide, and sandstone consists of particles of sand cemented together.

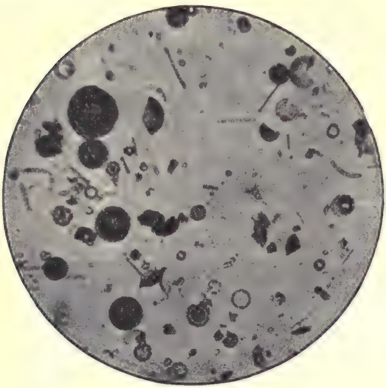


FIG. 99. — INFUSORIAL EARTH. HIGHLY MAGNIFIED.

Silica is found in most plants, especially in their stalks and stems. It imparts firmness to the stems and to the resistant exterior coating of straws, scouring rushes, and bamboo. Sponges, the quills of feathers, claws of animals, and the finger nails contain considerable silica.

339. Properties of Silicon Dioxide. — Silica is harder than glass; it is insoluble in ordinary reagents, but will dissolve in melted alkalies. Melted in the oxyhydrogen flame, quartz can be drawn into delicate elastic threads, which are used in scientific instruments.

340. Uses of Silicon Dioxide. — White sand, which is nearly pure silica, is used in making glass and porcelain.

Common sand is discolored by impurities, and if the particles are sufficiently irregular and angular it can be used in sandpaper and mortar. Sandstone is used for building; hard varieties are used for grindstones and millstones. Ground glass is glass that has been roughened by blowing sand against it by means of a blast of air. Many clear varieties of quartz are cut and polished for jewelry, as amethyst, agate, carnelian, false topaz, and imitation diamond. Clear rock crystal is cut for lenses. Petrified wood has been formed by the gradual replacement of the woody fiber by silica, preserving the woody appearance. Cut and polished petrified wood is used as an ornamental stone. The fine varieties of infusorial earth are used as abrasives in polishing powders, and are also used in cements, in refractory fire brick, and as an absorbent in dynamite. Quartz, melted by the oxyhydrogen flame or the electric furnace, is fashioned into tubes and dishes for use in the laboratory. This material is called *vitrified silica*. Silicon dioxide is used as a filler in paint.

341. Silicates. — Silica reacts with the hydroxides of the alkali metals, sodium and potassium, to form silicates:

water glass

$$SiO_2 + 2\,KOH \longrightarrow K_2SiO_3 + H_2O$$

Sodium and potassium silicates are soluble in water; nearly all the other silicates are insoluble, stable compounds, which comprise the larger part of the earth. Such minerals as feldspar, mica, hornblende, and clay are silicates. Various mixtures of these comprise the common rocks, as granite, gneiss, and slate.

Sodium and potassium silicates are made by heating to fusion the metallic hydroxides, or carbonates, with silicon dioxide. The thick water solution, called water glass, is

used in filling soaps, in making artificial stone and cement, in ready mixed paints, wall coloring, calico printing, and fireproofing wood and textiles.

Silicon dioxide is the anhydride of silicic acid:

$$SiO_2 + H_2O \longrightarrow H_2SiO_3$$

At high temperatures, silica combines directly with basic oxides, like calcium oxide (§ 390), to form silicates:

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

This action is the basis of the formation of *slag*, in the extraction of iron and other metals.

342. Glass. — Glass is a *mixture of silicates*. Common, crown, or window glass consists of silicates of sodium and calcium; Bohemian glass, of potassium and calcium silicates; flint glass contains silicates of lead or barium, and potassium.

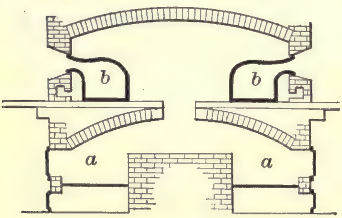
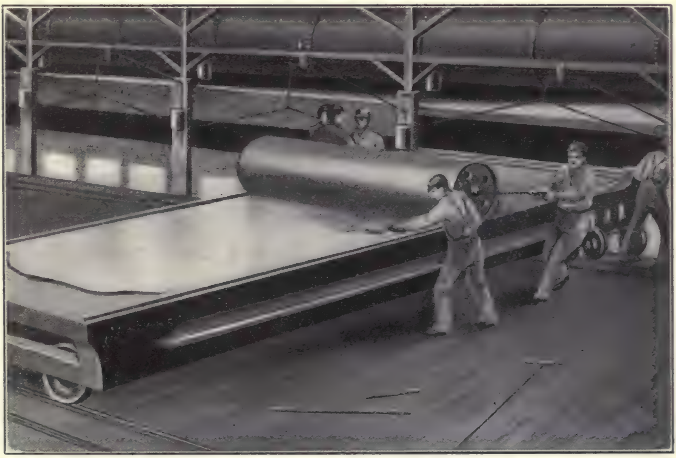


FIG. 100. — GLASS FURNACE.
a, fire-boxes; *b*, melting-pots.

Glass is made by melting together sand, an alkali, and calcium carbonate in pots of fire clay (Fig. 100) or tanks made of fire bricks. The alkali may be sodium or potassium carbonate or a mixture of these. An oxidizing agent, as potassium nitrate or manganese dioxide, may be added to remove the green color due to iron compounds. The mixture is heated to a high temperature and thoroughly melted; the gases that are given off, chiefly carbon dioxide, aid the mixing. The heating must continue long enough to expel all of the gas, or there will be bubbles or streaks in the finished glass. Any infusible impurities coming to

the top are skimmed off. When the mass is cooled to a pasty condition, it may be blown or molded.

Window glass is made by the workman taking a mass of the molten glass on the end of a long iron blowpipe, and blowing it into a large bubble. This is drawn out into a cylinder by swinging it and rolling it on a plate. The ends of the cylinder are cut off, a cut is made lengthwise, and the glass is spread out flat. *Plate glass* is made by



By courtesy of *The Scientific American.*

FIG. 101.—ROLLING OUT PLATE GLASS.

pouring the molten glass on a bronze table, rolling it with a hot iron cylinder (Fig. 101), and finally polishing it. *Cut glass* is flint glass molded to the desired shape; the design is cut by a wheel, and the glass polished with rouge or putty powder.

Cheap glass dishes and similar objects are made by pressing the plastic glass in a die. Bottles are blown in a mold. If the glass is cooled rapidly, it is hard, brittle, and liable to break under a shock. To overcome this it is

annealed, that is, the glass is passed slowly through a long, tunnel-like furnace from the hot to the cooler end, so that the temperature is very gradually lowered. This process often takes several days.

Crown glass is a colorless window glass used for convex lenses. *Bohemian glass* is harder and less fusible, and is used for chemical apparatus. *Flint glass* is brilliant, heavy, and soft, and is used for concave lenses, lamp chimneys, cut glass, and for imitation gems, such as paste diamonds.

Glass is colored by dissolving various substances in the melted mass. The green color of common glass is due to iron compounds in the sand and limestone; chromium compounds give a rich green. Compounds of copper and cobalt give blue color; manganese, pink to violet; manganese with iron, yellow to brown; silver, yellow; gold, ruby red; calcium fluoride, white and translucent.

343. Silicon Carbide, or Carborundum. — Silicon carbide, carborundum, is a crystallized solid varying in color, and often brilliant and iridescent. It is extremely hard, and is used as a substitute for emery for grinding and polishing in wheels, hones, and carborundum cloth (Fig. 102).

SiC

FIG. 102. — CARBORUNDUM PRODUCTS.

Carborundum is made in an oblong electric furnace, at the ends of which are metal plates to which are attached the heavy carbon electrodes projecting

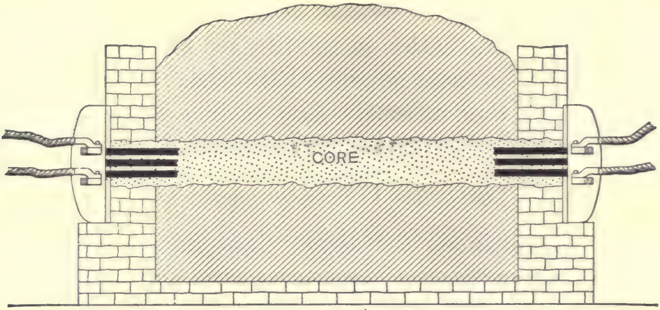


FIG. 103. — CARBORUNDUM FURNACE — SECTIONAL.

into the furnace (Fig. 103). The electric connection between the electrodes is through a mass of granulated coke.

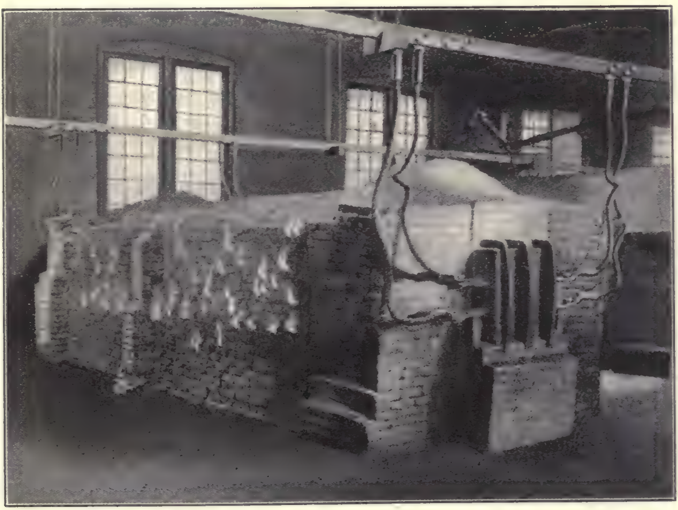


FIG. 104. — ELECTRIC CARBORUNDUM FURNACE.

Sand, a little salt, and sawdust are mixed with coke. The salt is used to aid fusion, and the sawdust to make the mass porous. This mixture is piled around the central core of

coke and held in place by side walls of loosely piled bricks (Fig. 104). The action in the furnace is not electrolytic, but is due to the heat generated through the resistance of the coke to the current. The carbon reacts with the melted sand to form carbon monoxide and carborundum:

$$SiO_2 + 3\,C \longrightarrow SiC + 2\,CO$$

The action continues for about eight hours. When the furnace has cooled, the sides are torn down and the carborundum removed. The best crystals are found around the central core. The crystals are crushed, washed with sulphuric acid, dried, and graded according to size.

344. Silicon fluoride, SiF_4, is a colorless gas formed in the reaction of hydrofluoric acid, HF, with silica, SiO_2, or with glass. It decomposes in water, forming hydrofluosilicic acid, H_2SiF_6, and silicic acid, H_2SiO_3.

345. Boron. — The element boron is of little importance. It is a brown powder, soluble in many melted metals, and infusible at the temperature of the electric arc. Its important compounds are boric acid and borax.

346. Boric acid, H_3BO_3, occurs in minute quantities in vapors arising from the earth in the volcanic regions of Tuscany, in Italy. Most of the boric acid used in the United States is made by the reaction of colemanite, impure calcium borate, with sulphuric acid.

Boric acid is obtained in fine crystalline scales. It is a weak acid, sparingly soluble in water. It is used as an antiseptic and as a preservative.

347. Borax. — Sodium tetraborate, $Na_2B_4O_7$, is the familiar compound, borax. In California there are large

deposits of impure borax and calcium borate, which supply this country.

Borax is obtained from solutions in large crystals, containing either 5 or 10 molecules of water of crystallization, according to the temperature at which they are deposited. Ordinary borax has the composition $Na_2B_4O_7 \cdot 10\ H_2O$. A solution of borax has a feeble alkaline reaction.

Borax is employed in large quantities as an antiseptic and preservative, and as a cleansing agent. In soldering and welding it is used to dissolve the metallic oxides.

348. Borax Bead Tests. — When heated, crystallized borax swells during the evaporation of the water of crystallization and then melts to a clear glassy mass. Fused borax dissolves metallic oxides, and these often impart to the glassy mass a color characteristic of the metal. Thus, cobalt compounds give a blue color, and manganese compounds a violet color, when heated with a drop of fused borax in the oxidizing flame.

SUMMARY

Silicon is a very abundant element which, in itself, is of little practical importance. **Silicon dioxide** (silica) is its most common compound, occurring as quartz and sand and as a constituent of many rocks.

Silica is very hard and fuses only at high temperatures. It is used in making glass, mortar, and polishing powders.

Silicates are salts of silicic acids. Sodium and potassium silicates are soluble.

Glass is a mixture of silicates. Three varieties are crown, flint, and Bohemian glass. The materials are melted together and blown or molded into shape while plastic. Colors may be added to it while in a melted state.

Silicon carbide is made by heating coke and sand in an electric furnace. It is used as an abrasive.

Boric acid is found in nature, but much of it is made from calcium borate.

Borax occurs in large deposits in California. It gives characteristic reactions with metallic oxides used as bead tests. Borax is used in soldering and welding, and as a preservative and cleansing agent.

EXERCISES

1. Why is it difficult to obtain silicon from its oxide?

2. Give the most important uses of silicon dioxide.

3. Why is sand the main final product of long-continued disintegration of rock materials by water?

4. What is water glass? How is it made, and what are its uses?

5. What is vitrified silica? Why should not basic substances be melted in silica ware?

6. Give the essential composition of a glass.

7. Give the composition and uses of the three chief varieties of glass.

8. Describe the manufacture of some one kind of glass.

9. Explain, using an equation, the production of carbon dioxide in glass making, and state how it is eliminated from the finished glass.

10. How is glass annealed? What is the effect of this process on the properties of the glass?

11. Explain, with the aid of an equation, the action of hydrofluoric acid on glass.

12. How does the composition of hard glass differ from that of soft glass?

13. Calculate the percentage of water of crystallization in borax.

CHAPTER XXVIII

CALCIUM AND ITS COMPOUNDS

CALCIUM

349. Although metallic calcium has been known for many years, it is only recently that it has been made in any quantity. Sir Humphry Davy was the first one to see the metal, but failed to get enough to determine its properties. The credit for the successful isolation of calcium belongs to Dr. Robert Hare, a scientist of Philadelphia. His electrolytic method, with some modifications, is the one now used to obtain the metal.

350. Preparation. — Metallic calcium is prepared by passing an electric current through fused calcium chloride contained in a crucible of graphite, which acts as the anode (Fig. 105). At first the cathode is an iron rod (*B*), capable of being raised by a screw mechanism (*A*). The calcium deposits on the end of the iron rod, solidifies, and grows downward as an irregular cylinder. This rod of calcium becomes the cathode (*C*) as the iron rod is gradually raised out of the molten chloride by the screw mechanism. A coating of calcium chloride protects the calcium from oxidation as it emerges from the molten bath. The electric current, by its passage, keeps the calcium chloride molten in the graphite crucible, except

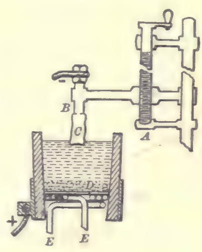


Fig. 105.

at the bottom (*D*), where it is kept cold and is solidified by water running through a copper coil (*EE*). The chloride adhering to the sticks of calcium is removed by hammering.

351. Physical Properties. — Pure calcium is a silver-white metal of brilliant luster, and is a little lighter than magnesium. It is harder than lead or tin, but softer than zinc. At 300° to 400° C. it is as soft as lead and can easily be rolled or hammered. Only a few metals surpass calcium as conductors of electricity.

352. Chemical Properties. — Calcium keeps its luster in dry air and can be preserved without difficulty in a stoppered bottle. In moist air its surface becomes dulled. Molten calcium burns vigorously in oxygen and in chlorine.

Water is *slowly* decomposed by calcium, and hydrogen is evolved at a rate very convenient for the collection of the gas:

$$Ca + 2\,H_2O \longrightarrow Ca(OH)_2 + H_2$$

CALCIUM CARBONATE

353. Occurrence. — Calcium carbonate, $CaCO_3$, is one of the most abundant compounds occurring in nature. In the form of limestone it constitutes whole mountain ranges. Marble, which exists in enormous quantities in various parts of the world, is a purer form of calcium carbonate than limestone. Marble was formed from limestone by the action of heat and pressure under such conditions that carbon dioxide, which generally is given off when limestone is heated, was prevented from making its escape.

The mineral matter in shells is chiefly calcium carbonate derived from the water in which the animals lived.

In past ages, deposits of shells became cemented together into rock materials. Coquina, or the loose shell rock of Florida, illustrates an early stage of this process (Fig. 106), and limestone a more complete transformation.

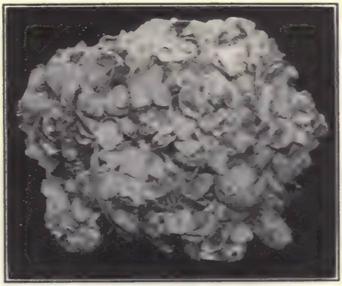


FIG. 106. — COQUINA.

Calcite is a pure crystalline form of calcium carbonate, and one of its varieties, Iceland spar, gives a double refraction of light (Fig. 107). In many other minerals, such as chalk and dolomite, calcium carbonate is present.

354. Properties. — When pure, calcium carbonate is a white solid, often transparent. The color of limestone and many varieties of marble is due to the presence of impurities. Calcium carbonate occurs naturally in amorphous masses and in crystals of different forms. When precipitated from solutions of calcium salts by soluble carbonates, it comes down at first as amorphous scales and later as minute crystals. It is only very slightly soluble in pure water, but, as we have already seen (§§ 328, 329), it is more soluble in water containing dissolved carbon dioxide.

FIG. 107. — ICELAND SPAR.

The hardness of water in limestone regions causes it to form a firmly adhering deposit on all vessels in which it is boiled, since boiling decomposes the calcium bicarbonate, driving off part of its carbon dioxide and leaving the insoluble carbonate. This deposit, known as *boiler scale*, is a

poor heat conductor, and clogs the tubes of steam boilers. Hence the water is often softened before being introduced into the boilers.

355. Limestone Caves. — The formation of underground caverns in limestone regions is due to the production, solution, and decomposition of the bicarbonate. Charged

FIG. 108. — STALACTITES AND STALAGMITES IN A LIMESTONE CAVE.

with carbon dioxide from decaying organic materials, the soil water dissolves limestone and sinks through cracks in the rocks, widening them as it goes. Reaching a less soluble stratum of rock, it flows along this, but dissolves the limestone above. This action, continuing for centuries, finally excavates a cave, such as Mammoth Cave in Kentucky and Luray Cavern in Virginia. As soon as these caves are hollowed out, a new process sets in. The water,

before it drops from the roof, loses some of its carbon dioxide, and part of the bicarbonate is converted into the insoluble carbonate. This is left behind on the roof of the cave. The drops that fall to the floor lose more carbon dioxide and some water by evaporation, and likewise deposit calcium carbonate. The final result of the process is the formation of hanging masses of calcium carbonate, like icicles of stone, known as *stalactites*, and the formation of round mounds below called *stalagmites* (Fig. 108). These in turn finally unite to form columns. In this way the cave may become nearly filled again.

356. Uses of Calcium Carbonate.—Natural calcium carbonate has three very important uses. Large quantities of limestone and marble are used as *building stone*. Enormous amounts of limestone are yearly "burned" (heated to expel the carbon dioxide) to form *quicklime*. Much limestone is used in the production of cast iron (§ 390). Ground limestone is frequently used on farm land, to neutralize undesirable acids that may be present in the soil.

CALCIUM OXIDE Quicklime

357. Manufacture of Lime. — Calcium oxide, or *quicklime*, is made by the decomposition of calcium carbonate at a red heat:

$$CaCO_3 \longrightarrow CaO + CO_2$$

The manufacture of lime is carried on

FIG. 109. — LIME KILN.

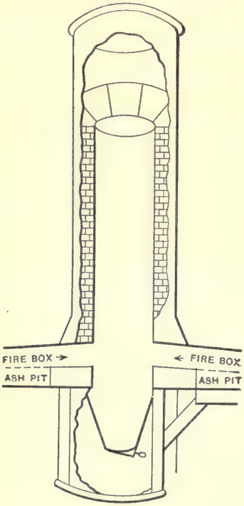


FIG. 110. — LIME KILN.

in special furnaces called *lime kilns* (Fig. 109). In the modern lime kilns (Fig. 110), the fire is in side chambers and only the hot gases find their way up through the charge of limestone fed in at the top of the furnace. In this *long flame process*, the lime withdrawn at the bottom of the kiln is free from ashes.

If the limestone contains impurities, as silica, iron, or alumina, in any considerable amount, a poor quality of lime is obtained. The successful operation of the kiln depends upon the efficient removal of the waste gases from the shaft, so that the carbon dioxide which is formed does not cause a reversal of the action. This constitutes a practical application of the law of mass action.

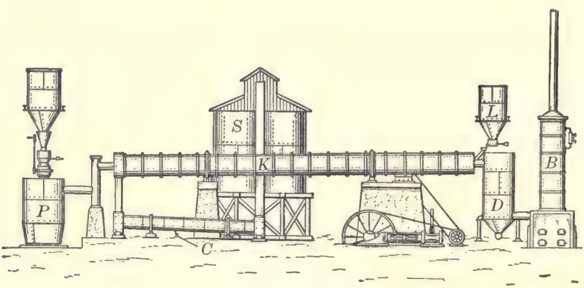


FIG. 111. — ROTARY LIME KILN.

P, gas producer; *K*, kiln; *L*, limestone bin; *D*, dust chamber; *B*, boiler; *C*, cooler; *S*, storage bin for lime.

358. Rotary Lime Kiln. — The best lime is made in a rotary kiln (Fig. 111), in which limestone, crushed to one-

inch pieces, slowly passes down the rotating cylinder and meets an intensely hot flame from the burning of a blast of hot air and producer gas (or pulverized coal). The flame extends a considerable distance into the kiln, and the intense heat completely expels the carbon dioxide from the pieces of limestone as they turn over and over. The hot lime at the lower end of the kiln drops into a rotary cooler. Here it gives up its heat to the air that is used for the kiln blast.

Heat economy is not only secured in this way, but also by passing the hot gases from the top of the kiln through the dust settling chamber to the boiler, where these gases generate all the steam necessary for the gas producer and for driving all the machinery connected with the kiln. Few manufacturing processes are operated with so complete utilization of the heat generated.

The rotary kiln produces a thoroughly and carefully burned lime, free from dust and ashes. Its small and uniform pieces permit compact packing, and for this reason the lime is less liable to air-slake than the larger lumps of varying size produced by other kilns. Moreover, it slakes with water more rapidly and evenly than lime made by other processes.

359. Properties. — Pure calcium oxide is a soft, white, non-crystalline substance which can only be fused and vaporized at the temperature of the electric arc (about 3500°).

It slowly takes up moisture, forming the hydroxide:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

When water is put on lumps of quicklime, cracks soon appear on the surface, the mass swells, and finally falls to a voluminous white powder. The heat of combination is

so great that the lime becomes hot, and clouds of steam arise. This energetic action or process is called *slaking*, and the product of the reaction, calcium hydroxide, is called *slaked lime*. When quicklime is left exposed to the air, both water and carbon dioxide are taken up, with the formation of both calcium hydroxide and calcium carbonate. This process is known as *air-slaking*.

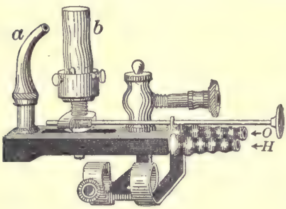


FIG. 112.—LIME-LIGHT BURNER.

360. Uses. — On account of its infusibility and dazzling incandescence in the oxyhydrogen flame, the oxide is used in the calcium or lime light. A lime-light burner is shown in Fig. 112; *a* is the burner tip for an oxyhydrogen flame, and *b* is the cylinder of quicklime. Many other uses of calcium oxide are considered in connection with the hydroxide.

CALCIUM HYDROXIDE

361. Properties and Uses. — Calcium hydroxide, or slaked lime, is a soft white solid when pure, and is sparingly soluble in water, forming a solution called *limewater*. Limewater, white with suspended but undissolved particles of the hydroxide, is known as *milk of lime*.

When heated, the hydroxide loses water and is reconverted into the oxide, showing the reaction to be a reversible one, according to the temperature:

$$Ca(OH)_2 \rightleftarrows CaO + H_2O$$

The water solution of calcium hydroxide is strongly basic, a property which has led to the wide use of the hydroxide as a cheap alkali. In this respect it stands among the bases as sulphuric acid does among the acids.

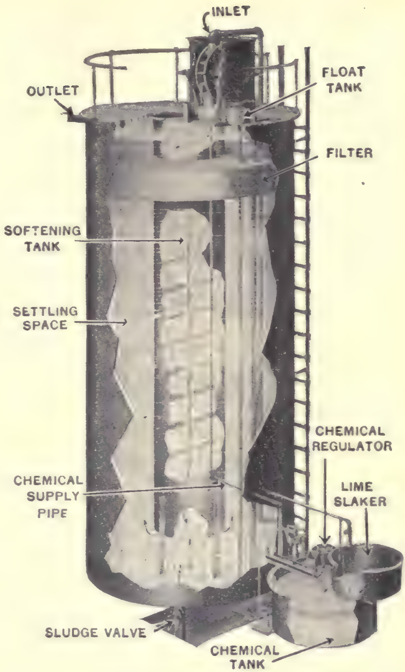


FIG. 113. — WATER SOFTENING APPARATUS.

Lime, as a cheap base, is used in the manufacture of alkalies and bleaching powder, in glass making, for whitewash, in the removal of hair from hides, and in many other industries. It is employed in water softening. In one process of water softening, the slaked lime is thoroughly mixed with water in the chemical tank (Fig. 113), and then fed into the top of a long, vertical softening tank. Revolving paddles in this tank thoroughly mix the lime with the water to be softened, and the following reaction takes place:

$$CaH_2(CO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3 + 2\,H_2O$$

As the water passes out of the bottom of the softening tank and up through the larger tank surrounding it, most of the calcium carbonate and other solid impurities settle out. Any remaining solids are removed by the filter, and the softened water flows from the outlet at the top. If the water contains permanent hardness, sodium carbonate is used with the lime. The chief use of lime, however, is in the preparation of mortar and cement.

362. Mortar. — When sand is thoroughly mixed with wet, freshly slaked lime, ordinary mortar is produced. Mortar is employed to form a hard, stony mass, which holds together the stones or bricks in a building. The hardening of the interior of mortar is chiefly due to the escape of water. The slaked lime forms a kind of jelly-like mass with the water, in which the grains of sand are entangled. As the water evaporates, the calcium hydroxide sets into a compact, stony mass, and the sand gives additional strength. At the outer surface of the mortar, which is exposed to the air, the calcium hydroxide reacts with the carbon dioxide of the air, forming calcium carbonate:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

This action takes place slowly, and forms a hard protective outer layer, which prevents water from again entering the mortar and softening the calcium hydroxide. Good mortar increases in strength with age, as the solidity of buildings erected centuries ago shows. Cement is now frequently used in place of part or all of the lime in mortar.

CALCIUM SULPHATE

363. Varieties. — Calcium sulphate is, next to the carbonate, the most abundant and widely distributed salt of calcium. It occurs as the mineral anhydrite, $CaSO_4$, and as gypsum, $CaSO_4 \cdot 2\,H_2O$. Satinspar, alabaster, and selenite are varieties of gypsum. Selenite is often found in large, transparent crystals, so soft that they can be scratched with the finger nail. Gypsum is used for the same purpose as limestone in improving soils.

364. Plaster of Paris. —Gypsum is but sparingly soluble in water; its solubility increases to 40° and then decreases.

When heated to the proper temperature, gypsum loses three quarters of its water of crystallization, and the residue may be said to have one molecule of water of crystallization to every two molecules of calcium sulphate, $(CaSO_4)_2 \cdot H_2O$. The chalky powder resulting from the heating is known as *plaster of Paris*. On a large scale it is made by heating in kilns a charge of gypsum broken into small lumps to insure evenness in "burning." Care is taken not to overheat; 125° C. is the most favorable temperature for the process.

365. Plaster Casts. — When plaster of Paris is wet, water is again taken up, forming needles of crystallized gypsum which, becoming entangled, set or form a hard mass. The hardening is also accompanied by a slight increase in volume. This property explains the use of plaster of Paris in making casts. The slight expansion secures a sharp impression of the mold. The powder is mixed with about a third its weight of water, the pasty mass put into the mold, and in less than half an hour the plaster sets. The ivory surface of casts is secured by dipping them in melted paraffin or by painting them with a solution of paraffin in petroleum ether. The solvent in the latter case evaporates, leaving the waxy filling in the pores of the cast and making it impervious to water. Many beautiful ornamental objects are now made by plating a thin film of metal on a plaster of Paris base. Plaster of Paris is also used for rigid bandages in surgery and as a surface coating for walls. *Stucco* is plaster of Paris and rubble, mixed with sizing or glue instead of water.

366. Calcium Phosphates. — The phosphates of calcium are of great importance to organic life. The mineral matter in bones of animals is essentially *normal calcium*

phosphate, $Ca_3(PO_4)_2$. This compound occurs as phosphorite, which has been derived from animal remains. *Guano* contains phosphates in addition to nitrogenous compounds. Phosphates are an important plant food, but to be available must be in a soluble form that can be taken up by the plants. The soluble phosphates result from the decomposition of rocks containing phosphates. Since the process is a slow one, the supply of soluble phosphates in cultivated soils often becomes scanty. To supply this need, the manufacture of soluble phosphates for fertilizers has grown to be an important industry.

The monocalcium phosphate, or *superphosphate of lime*, $CaH_4(PO_4)_2 \cdot 2\,H_2O$, is the most important artificial fertilizer. It is made by treating rock phosphates with crude sulphuric acid. The superphosphate formed is readily soluble in water, and when spread upon the soil is available for plant use. The superphosphate is also used in baking powders.

367 Bleaching Powder. — Bleaching powder, or chloride of lime, is made by passing chlorine over freshly slaked lime spread on the floors of a series of absorption chambers (Fig. 114). Chemists are still in doubt as to the reactions involved in the process and the formula of the product. The latter, however, is often represented as $CaOCl_2$.

FIG. 114.

Bleaching powder is an unstable white powder which is slightly soluble in water. When bleaching powder is treated with acids, chlorine is evolved. Hence the powder is used as a source of chlorine for bleaching purposes.

The cotton to be bleached is freed from grease and oil. The cloth is next soaked in a solution of bleaching

powder, then dipped in dilute acid, and finally thoroughly washed to remove the chemicals (cf. § 80). The solutions used are very weak, to prevent injury to the fiber of the cloth.

When exposed to the air, bleaching powder slowly reacts with the carbonic acid formed by the union of carbon dioxide with water. As a result chlorine is liberated, and for this reason the powder, often called *chloride of lime*, is used as a disinfectant and germicide.

SUMMARY

Calcium, although very abundant in nature, is rarely seen as metal.

It can be obtained by the electrolysis of fused calcium chloride.

The most important **calcium compounds** are:

the carbonate (limestone, chalk, marble);

the hydroxide (slaked lime);

the oxide (quicklime);

the phosphate (phosphorite);

the sulphate (gypsum).

Lime is made by heating calcium carbonate. **Slaked lime** is made by adding water to quicklime. **Air-slaked lime** is a mixture of calcium hydroxide and calcium carbonate, formed by the exposure of quicklime to air.

Slaked lime is used in making mortar, which hardens by the evaporation of water and the absorption of carbon dioxide.

Plaster of Paris is made by partly dehydrating gypsum. It is used in making plaster casts.

Calcium phosphates, derived from bone ash and rock deposits are used in making fertilizers.

Bleaching powder is made by passing chlorine over slaked lime It is used in bleaching and as a disinfectant.

EXERCISES

1. Write the equation for the reaction between water and (*a*) sodium, (*b*) calcium. How do the reactions differ in intensity?

2. What is the "fur" deposited in tea kettles in which hard water is boiled?

3. Explain the formation of stalactites and stalagmites.

4. How much quicklime can be obtained from 4 tons of limestone containing 98 % of calcium carbonate?

5. Why is the production of lime hastened by blowing air or steam into a lime kiln?

6. In the laboratory, loosely stoppered bottles that contain quicklime are sometimes found with the sides broken out. How do you account for this?

7. Write the equations that illustrate the formation of air-slaked lime.

8. What weight of water enters into combination in slaking 500 lb. of quicklime?

9. Lime water standing exposed to air becomes coated with a film of insoluble substance. What is the substance? Explain its formation.

10. How could quicklime be made from slaked lime?

11. What weight of nitric acid would be required to neutralize 35 grams of calcium hydroxide?

12. Compare the hardening of mortar with that of plaster of Paris.

13. For what reason is normal calcium phosphate converted into "superphosphate" in the manufacture of fertilizers?

14. Why is bleaching powder shipped in air-tight containers?

15. Account for the disinfecting power of "chloride of lime."

16. Calculate the weight of quicklime that one might expect to get from 1000 kilograms of pure limestone. What weight of carbon dioxide would be given off during the action? What volume would the gas have, standard conditions?

CHAPTER XXIX

MAGNESIUM, ZINC, AND MERCURY

MAGNESIUM

368. Occurrence and Preparation. — Although magnesium is of comparatively little commercial importance, its compounds are very abundant in nature. The most important of these are *dolomite*, a double carbonate of calcium and magnesium ($CaCO_3 \cdot MgCO_3$); *magnesite* ($MgCO_3$); *carnallite*, a double chloride of potassium and magnesium ($KCl \cdot MgCl_2 \cdot 6\,H_2O$); *kainite*, a double salt of potassium chloride and magnesium sulphate ($KCl \cdot MgSO_4 \cdot 3\,H_2O$). Magnesium is also found in combination with other elements in various natural silicates, for example, hornblende and asbestos. ***Epsom salts***, magnesium sulphate ($MgSO_4 \cdot 7\,H_2O$), is found in some springs whose waters owe their laxative properties to its presence.

The metal is commercially obtained by the electrolysis of carnallite. The salt is fused, together with some common salt or cryolite, in an iron crucible which acts as the cathode. A carbon rod serves as the anode.

369. Properties and Uses. — Magnesium is a silvery white metal of low specific gravity. It resembles both calcium and zinc in its properties, and stands between them in metallic character. It decomposes water slowly at 100°, but does not affect it at ordinary temperatures. Moist air acts on magnesium slowly, forming a basic carbonate of magnesium. Magnesium burns with comparative ease,

with the evolution of a brilliant white light of great actinic power. The oxide is formed by this reaction:

$$2\,Mg + O_2 \longrightarrow 2\,MgO$$

Dilute acids react with magnesium very readily, hydrogen usually being evolved.

Magnesium is one of the few elements that enter into direct combination with nitrogen. When nitrogen is passed over red-hot magnesium, magnesium nitride, Mg_3N_2, is formed.

Magnesium is sometimes used in flashlight preparations for photographic purposes because of the actinic power of the light it gives in burning. It is also used in making fireworks, and certain light alloys.

370. Compounds of Magnesium. — The common salts of magnesium are stable substances and, with the exceptions of the carbonate and the phosphate, are soluble in water. The formulas of the magnesium compounds show that the element has a valence of two, or we may say it forms bivalent ions.

Mixtures of magnesium carbonate with magnesium hydroxide are used in pharmaceutical preparations and in face powders.

The acetate, bromide, citrate, and sulphate of magnesium are valued on account of their medicinal properties. The sulphate is the medicinal constituent of many commercial laxative waters. Magnesium chloride is used to some extent for fireproofing materials and in the manufacture of disinfectants.

Many magnesium compounds, when heated in an oxidizing flame, are converted into magnesium oxide. This, when moistened with a solution of cobalt nitrate and heated, yields a mass having a pale pink color.

ZINC

371. Minerals are the elements and compounds whose mixtures make up the inorganic material of the earth. Copper, sulphur, rock salt (NaCl), silica (SiO_2), calcite ($CaCO_3$), and hematite (Fe_2O_3) are examples of minerals.

372. Ores are the natural deposits from which elements, especially the metals, are extracted. An ore is seldom composed of a single mineral.

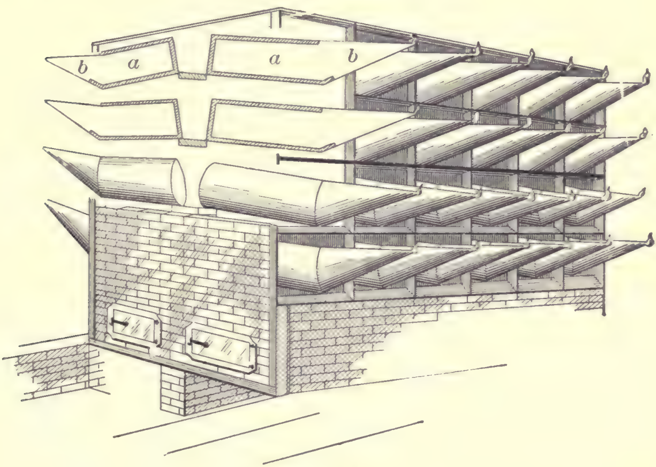


FIG. 115.

373. Extraction from Ores. — Zinc is not found in the uncombined state. Some of its common ores are zinc blende, ZnS; smithsonite, $ZnCO_3$; zincite, ZnO.

To separate zinc from the oxide, the ore is finely powdered and mixed with coal. The mixture is then heated in earthenware retorts (Fig. 115, *a*). The carbon reduces the zinc oxide:

$$ZnO + C \longrightarrow Zn + CO$$

The temperature in the process is raised above the boiling point of the metal, 950°, which therefore passes off as a gas, and is condensed in earthenware or iron receivers (*b*).

When the ore is not an oxide, a preliminary operation must precede the reduction. This consists in heating the ore on grates in contact with air. The operation is known as *roasting*, and converts the metal into an oxide. In the case of zinc sulphide, care is taken not to convert it into the sulphate.

$$ZnCO_3 \longrightarrow ZnO + CO_2$$
$$2\,ZnS + 3\,O_2 \longrightarrow 2\,ZnO + 2\,SO_2$$

The oxide that results in these reactions is then reduced with the carbon in the manner that has been described. The silicate is reduced directly.

Zinc, as extracted from its ores, usually contains carbon, arsenic, cadmium, and other impurities. It is freed from these by distillation.

374. Physical Properties. — Zinc is bluish white in color. It comes into the market in the form of heavy bars, called *ingots* or *spelter*, formed by pouring the melted metal into molds. In this form, the metal is crystalline in structure and rather brittle. Between 100° and 150° C. it is malleable and ductile, and can be rolled into sheets. After having been obtained in this form, it remains malleable at ordinary temperatures. At 300° it again becomes brittle and can be powdered.

Granulated or *mossy* zinc is a form much used in the laboratory. It is made by pouring the melted metal into water. *Zinc dust* is obtained by the distillation of the metal. As long as the receiver remains comparatively cold, the distilled zinc collects in the form of a powder. This operation is similar to the one by which sulphur is

obtained as flowers of sulphur. Zinc dust always contains a certain amount of the oxide.

375. Chemical Properties. — Zinc is regarded as distinctly metallic, but it differs considerably from such metals as calcium and sodium. It resembles magnesium more closely. Zinc does not act on water at ordinary temperatures. Air attacks it slowly in the presence of moisture, forming a basic carbonate, which acts as a protective coating, so that only the outer layer of the metal is affected. When zinc is heated in air or oxygen, it burns with a bluish flame, forming zinc oxide:

$$2\,Zn + O_2 \longrightarrow 2\,ZnO$$

Zinc reacts readily with dilute acids, forming zinc salts, and, as a rule, liberates hydrogen :

$$Zn + 2\,HCl \longrightarrow ZnCl_2 + H_2$$
$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

In acting on zinc (or other metals) nitric acid and concentrated sulphuric acid do not liberate hydrogen, since they act as oxidizing agents and convert the hydrogen into water. In these cases, the gases that are given off are reduction products of the acids.

The action of dilute acids on zinc is hastened by the presence of certain solid substances in contact with the metal. Pure zinc will scarcely react with acids, but if it is impure, solution takes place with great rapidity. A similar effect is produced by the presence of a very small amount of copper, or other metal, as a deposit on the surface of the zinc. In these cases the particles of carbon or copper act like cathode plates of a voltaic cell. Hence the velocity of the evolution of hydrogen from acids is increased by their presence.

Zinc reacts with solutions of potassium hydroxide to form potassium zincate and hydrogen:

$$Zn + 2\,KOH \longrightarrow K_2ZnO_2 + H_2$$

When hydrochloric acid is added to potassium zincate, zinc hydroxide is first formed and then reacts with an excess of hydrochloric acid to form zinc chloride.

Many compounds of zinc, when heated on charcoal or on a plaster of Paris block before a blowpipe, yield zinc oxide, yellow when hot, and white when cold. If the oxide is moistened with a drop of a solution of cobalt nitrate, and again heated, a bright green mass containing a compound of zinc and cobalt oxides is obtained.

376. Uses. — Zinc is used in making several important alloys. *Brass* is composed of copper and zinc; *German silver* contains copper, zinc, and nickel; *bronze* sometimes contains zinc in addition to copper and tin.

Galvanized iron is iron covered with a thin layer of zinc, which acts as a protective coating and prevents rusting. The old process for galvanizing consists of thoroughly cleaning the iron by immersing (pickling) it in an acid solution to remove rust, treating it with some other cleaning solution, and then dipping it into molten zinc. The zinc forms an alloy with the surface of the iron. A more recent process for galvanizing consists in plating the iron with zinc. The electrolytic bath generally consists of a solution of either zinc sulphate, or zinc sulphate mixed with other salts. Another use of zinc is for the anode plates of batteries.

377. Zinc Oxide and Hydroxide. — Zinc oxide, ZnO, is much used as a white pigment for paints. It does not have as great covering power as white lead, but it has the

advantage of not turning black from contact with hydrogen sulphide. It can be made by burning zinc or by heating zinc hydroxide or zinc carbonate :

$$Zn(OH)_2 \text{ (heated)} \longrightarrow ZnO + H_2O$$
$$ZnCO_3 \quad \text{(heated)} \longrightarrow ZnO + CO_2$$

A mixture of zinc oxide and white lead is considered preferable to the use of either alone, as zinc oxide scales, while white lead powders or chalks on being exposed to the weather. In paints containing a mixture of zinc oxide and white lead, these two tendencies counteract each other to some extent and the paint is made more durable.

On adding potassium hydroxide to a solution of a zinc salt, zinc hydroxide is precipitated, since this substance is insoluble in water. If an excess of potassium hydroxide is added, the hydroxide is dissolved, forming potassium zincate :

$$ZnCl_2 + 2\,KOH \longrightarrow 2\,KCl + Zn(OH)_2$$
$$Zn(OH)_2 + 2\,KOH \longrightarrow K_2ZnO_2 + 2\,H_2O$$

378. Salts of Zinc.—*Zinc chloride*, $ZnCl_2$, is obtained by the action of hydrochloric acid and zinc. It is an extremely deliquescent substance, sometimes used as a drying agent. It also has the power to dissolve metallic oxides ; because of this property its solutions make good soldering fluids for metals. Wood that has been soaked in a solution of zinc chloride resists decay. Zinc chloride is also used as a solvent for cellulose.

Zinc sulphate, $ZnSO_4$, is used in making battery solutions.

Zinc sulphide, ZnS, found in nature as zinc blende, can be prepared by the direct combination of zinc dust and sulphur, or it can be precipitated from solutions of zinc salts by the addition of hydrogen sulphide :

$$ZnCl_2 + H_2S \longrightarrow ZnS + 2\,HCl$$

But this reaction is reversible; that is, zinc sulphide will dissolve in dilute hydrochloric acid with the formation of zinc chloride and hydrogen sulphide:

$$ZnS + 2\,HCl \longrightarrow ZnCl_2 + H_2S$$

For this reason, the reaction shown in the first equation is never complete; for when a certain amount of hydrochloric acid has been formed, the second reaction begins to take place. This condition is a good illustration of the operation of the law of mass action (§ 168). Hydrogen sulphide is only slightly ionized, but its ions are necessary for the first reaction. If, however, a strong acid is present, its hydrogen ions increase the total concentration of the hydrogen ions to such an extent that the dissociation of the hydrogen sulphide is greatly lessened. Hence the number of sulphur ions becomes very small, and there is but little tendency to form the sulphide. If we dispose of the hydrogen ions as fast as they are formed, by adding such a substance as ammonium hydroxide, the precipitation of the zinc sulphide will be complete. If, on the other hand, much acid is present in the solution, the precipitation will be entirely prevented.

All soluble zinc salts are poisonous.

MERCURY

379. Occurrence and Separation. — Mercury is found only in a few localities, the deposits of Spain, Italy, Austria-Hungary, and the United States being the more important. The chief ore of mercury is *cinnabar*, HgS. Mercury is obtained from cinnabar by heating in contact with air (roasting) in order to convert the sulphur into sulphur dioxide and to vaporize the mercury:

$$HgS + O_2 \longrightarrow Hg + SO_2$$

The crude mercury vapor thus obtained is condensed and purified.

380. Physical Properties. — At ordinary temperatures, mercury, commonly known as *quicksilver*, is a silvery-white liquid, with a brilliant metallic luster. Its density is greater than that of lead, so that iron easily floats on it. Mercury solidifies to a substance resembling tin at about $-40°$ C, and boils at a temperature below red heat, but vaporizes slowly at ordinary temperatures. It is a good conductor of electricity. The molecular weight of mercury, as found from its vapor density, is the same as the atomic weight, 200; hence there is one atom in the molecule of mercury vapor.

The vapor of mercury is highly poisonous, as is the metal itself when finely divided. Mercury can be obtained as a fine gray powder by shaking it violently with flour, grease, or any substance that will coat the minute drops and prevent them from uniting to form a fluid mass. This process, known as *extinguishing*, is used in the preparation of blue pills and mercurial ointments.

381. Amalgams. — Mercury has the power of dissolving many other metals, forming alloys with them called *amalgams*. Mercury dropped on a gold ring will whiten it by amalgamating with the gold. These amalgams are not true compounds, as they have a varying composition. When there is a large excess of mercury, amalgams are liquid; otherwise they are solid.

382. Chemical Properties. — Mercury combines readily with the halogens and sulphur. Oxygen does not combine with it at ordinary temperatures, but at high temperatures it forms oxides, which at still higher temperatures

dissociate into mercury and oxygen. This is shown by the reversible equation:

$$2\,Hg + O_2 \rightleftarrows 2\,HgO$$

Pure dilute acids do not attack mercury. Concentrated nitric acid dissolves it readily, and dilute nitric acid also attacks it in the presence of nitrogen peroxide. Zinc and copper displace mercury from solutions of its salts and furnish a simple means of testing for a soluble salt of mercury.

383. Uses. — Mercury is used in important scientific instruments, such as the thermometer and barometer. It is also used for the collection of gases soluble in water. Its most important uses, however, are in the various amalgams. Amalgams of silver and other metals are used in filling teeth. Gold and silver are extracted by allowing the crushed ore to flow in a thin mud over tables covered with mercury. The gold amalgamates with the mercury, from which it can be separated by distilling the mercury.

Other uses of mercury and its compounds are in the manufacture of fulminates for explosive caps, in electrical appliances, and in the preparation of paints.

COMPOUNDS OF MERCURY

Mercury forms two series of compounds, the mercurous and the mercuric. The chlorides are the most important salts, and may be taken as typical of the two series.

384. Mercurous Chloride, known as *calomel*, has its composition represented by the formula HgCl. Since it is insoluble in water, it may be prepared by treating a solution of a mercurous compound with a chloride. It is produced

commercially by heating a mixture of mercuric chloride and mercury:

$$HgCl_2 + Hg \longrightarrow 2\,HgCl$$

Mercurous chloride is a white powder. Exposed to the light, it slowly blackens on account of the liberation of mercury by the reversal of the above reaction. It is extensively used in medicine.

385. Mercuric Chloride. — The common names of *mercuric chloride* are *corrosive sublimate* and bichloride of mercury. Its formula is $HgCl_2$. Mercuric chloride is made by heating a mixture of sodium chloride and mercuric sulphate; the chloride sublimes, as its name indicates. The sublimate is a white, translucent mass, from which the salt can be obtained in silky needles by dissolving in water and recrystallizing. It is slightly soluble in water at ordinary temperatures, but at higher temperatures it is more soluble. *Corrosive sublimate is a violent poison.* It is also a powerful antiseptic and germicide. For this purpose, very dilute solutions are used (1 part to 1000 parts of water). With the alkaline chlorides it forms double salts more soluble than mercuric chloride by itself, and much used in making antiseptic solutions.

386. Other Compounds. — The nitrates of mercury are the soluble mercury compounds most frequently met in the laboratory. Mercuric oxide is used in the preparation of paints for ship bottoms. These paints are sufficiently poisonous to prevent the fouling of the bottom by marine growths. Mercuric sulphide forms when hydrogen sulphide is added to a solution of either a mercurous or a mercuric salt. If mercurous sulphide is first formed, it decomposes into a mixture of mercuric sulphide and mercury. *Vermilion* is mercuric sulphide.

MAGNESIUM

SUMMARY

Atomic weight 24. Valence 2.

Magnesium is of little commercial importance. It is **used** in making several light alloys, in fireworks, and in flashlight powders.

When heated, magnesium combines directly with nitrogen.

Common magnesium salts, with the exceptions of the carbonate and phosphate, are soluble in water.

Several magnesium salts are used **in medicine**.

The **carbonate** and the **hydroxide** are used in face powders and in the manufacture of other pharmaceutical preparations.

Magnesium chloride is used for fireproofing materials.

Epsom salts is crystallized magnesium sulphate, $MgSO_4 \cdot 7\ H_2O$.

EXERCISES

1. For what is magnesium used?

2. Magnesium oxide is slightly soluble in water. Would the solution give an alkaline or an acid reaction? Why?

3. What reaction takes place when dilute sulphuric acid is added to magnesium?

4. Mention two ways by which carbon dioxide could be obtained from magnesite.

5. What is Epsom salts?

6. How many grams of magnesia, MgO, could be prepared by heating 20 grams of magnesium carbonate? How many liters of carbon dioxide would be liberated?

7. When 0.362 gram of magnesium was added to an excess of dilute hydrochloric acid, 365 c.c. of hydrogen was liberated. At the time the measurement was made, the temperature was 21° C. and the pressure was 770 mm. From the data given calculate the hydrogen equivalent of magnesium.

ZINC

SUMMARY

Atomic weight 65. Valence 2. Melting point 419°. Boiling point 918°.

A mineral is an inorganic element or compound found native in the earth.

An ore is a substance that is mined because it contains a mineral from which some useful element, generally a metal, can be extracted.

Zinc is usually **obtained** by roasting the ore, to produce zinc oxide, and then reducing the oxide.

Spelter, sheet zinc, granulated or mossy zinc, and zinc dust are **commercial forms** of zinc.

Brass and German silver are common **alloys** of zinc.

Zinc is a **dualistic element**, since it acts like a metal with acids and like a non-metal with strong bases.

Zinc hydroxide acts as a base in the presence of strong acids and as an acid in the presence of strong bases.

Zinc oxide is used in the preparation of zinc ointment; it is also used as a substitute for white lead as a paint pigment.

Zinc chloride is used to clean metals preparatory to soldering; as a wood preservative; as a solvent for cellulose.

Zinc sulphide is white.

Zinc sulphate is used in the preparation of battery fluids and in the manufacture of fireproof paints.

EXERCISES

1. Starting with zinc carbonate, describe the preparation of four commercial forms of zinc.

2. Name two alloys of zinc and tell what each contains.

3. What is galvanized iron?

4. Why does zinc corrode very slowly in air?

5. What advantage is there in using zinc oxide (zinc white) in place of white lead for a paint pigment?

6. Name a compound that would form zinc hydroxide on the addition of the right amount of hydrochloric acid.

7. Write equations showing how hydrogen could be produced by the reaction of either an acid or a base with zinc.

8. Why is wood sometimes impregnated with a solution of zinc chloride?

9. Why is tin plate, preparatory to soldering, often wet with a solution of zinc chloride?

10. Mention two ways by which zinc sulphide can be formed.

11. Why will not hydrogen sulphide completely precipitate zinc, as zinc sulphide, from a solution of zinc sulphate?

12. Explain the fact that water solutions of zinc sulphate give an acid reaction.

13. Describe a test for zinc.

14. How many grams of zinc would be required to replace the hydrogen contained in 15 grams of sulphuric acid? How many liters of hydrogen would be formed?

MERCURY

SUMMARY

Atomic weight 200. Valence 1 or 2. Melting point − 39°. Boiling point 357°. Specific gravity 13.6.

Mercury **occurs** as the sulphide, from which it is extracted by roasting.

It is the only metal that is a **liquid** at ordinary temperatures.

Mercury **combines** readily with sulphur and the halogens. It combines with oxygen at temperatures a little below its boiling point. Concentrated nitric acid is the only acid that has much effect on mercury at ordinary temperatures.

Mercury is **used** in scientific and electrical instruments; in the preparation of pigments and amalgams, and for the extraction of gold.

Calomel, mercurous chloride, is used in medicine.

Corrosive sublimate, bichloride of mercury, or mercuric chloride, is a deadly poison and is used as a germicide.

EXERCISES

1. Write the equation for the extraction of mercury from cinnabar.

2. What properties of mercury make it suitable for use in thermometers? In barometers?

3. What is an amalgam?

4. Under what circumstances is it desirable to collect a gas by the displacement of mercury? Why is it more difficult to collect a gas by the displacement of mercury than by the displacement of water?

5. What would be a simple way of testing a solution for the presence of a mercury salt?

6. Why is mercuric oxide used in paints for ship bottoms?

7. Calculate the percentage composition of the two chlorides of mercury. What law is illustrated by the composition of these compounds?

8. Why do surgeons often wash their hands in a solution of mercuric chloride before performing an operation?

9. Why should bichloride of mercury tablets never be kept in a medicine closet?

CHAPTER XXX

IRON AND STEEL

387. Occurrence of Iron. — A consideration of the enormous quantity of iron used annually for an almost unlimited number of purposes, will show how impossible our present civilization would be without this metal.

Native iron occurs in igneous rocks in pieces varying in size from small grains to that of a mass found in Greenland which weighed more than a ton. As iron rapidly corrodes when exposed to moist air, native iron is not of common occurrence, but compounds of iron are common. The red and yellow colors of soils are generally due to oxides and silicates of iron. Nearly all meteorites contain iron alloyed with nickel. The principal ore of iron is hematite mixed with other minerals, such as silica and clay.

388. Formation of Iron Deposits. — When water percolates through a soil containing much vegetable matter, it takes up substances capable of reducing ferric compounds to ferrous compounds. When water containing carbon dioxide comes in contact with the ferrous compounds, ferrous acid carbonate, $FeH_2(CO_3)_2$, is formed, which is soluble. In this way iron is dissolved out of the soil. If water containing acid ferrous carbonate collects in a warm place *not in contact with air*, carbon dioxide is driven off and ferrous carbonate (siderite), which is insoluble in water, may be deposited. When water con-

taining ferrous acid carbonate is ***exposed to the air***, ferric hydroxide is formed:

$$4\ FeH_2(CO_3)_2 + 2\ H_2O + O_2 \longrightarrow 4\ Fe(OH)_3 + 8\ CO_2$$

This may be deposited, and, on becoming dry, may lose sufficient oxygen and hydrogen in the form of water to convert it into hydrated ferric oxide (limonite), $2\ Fe_2O_3$ $3\ H_2O$, or into ferric oxide (hematite), Fe_2O_3:

$$4\ Fe(OH)_3 \longrightarrow 2\ Fe_2O_3 \cdot 3\ H_2O + 3\ H_2O$$
$$2\ Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\ H_2O$$

389. Smelting is a general term used to designate one or more operations carried on in a furnace for the purpose of obtaining an element (nearly always a metal) from an ore.

390. Smelting of Iron Ore. — When impure hematite, for example, is to be smelted, it is necessary to accomplish *two* main operations. These are: (*a*) to reduce the oxide, for which purpose carbon in the form of coke is used; and (*b*) to separate the other minerals that occur in the ore; for this purpose a substance called a *flux* is employed. The flux also aids in the fusion of the ore.

When the ore contains sand (silica, SiO_2), limestone is used as a flux. On being heated in the furnace, the limestone is decomposed into carbon dioxide and calcium oxide:

$$CaCO_3 \longrightarrow CO_2 + CaO$$

The basic oxide, CaO, combines with the acidic oxide, SiO_2, and forms calcium silicate.

If the ore contains basic material, silicon dioxide may be used as a flux, and the removal of the impurity be effected in a way analogous to that just described.

391. Manufacture of Cast Iron. — Iron ores are smelted in a *blast furnace* (Fig. 116) which has a steel shell from 75 to 90 feet high, lined with a thick layer of fire brick. Cold water is made to circulate through hollow castings built into the fire brick in the part of the furnace where the most energetic chemical action takes place during the smelting. This is just above the point where pipes called *tuyères* admit powerful blasts of hot, dry air into the furnace. The name "blast furnace" is due to these blasts of air.

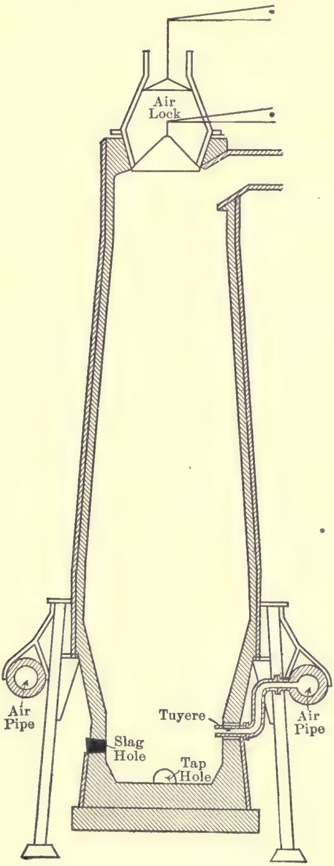


FIG. 116.—BLAST FURNACE.

A blast furnace, once started, is kept in continuous operation day and night, seven days in the week, until it is necessary to shut down in order to make repairs. The charge of ore, coke, and flux is dropped in at the top of the furnace from time to time. The heated blast of air which enters the furnace through the tuyères comes in contact with the burning coke and forms carbon dioxide, which is immediately reduced to carbon monoxide by the excess of hot carbon. The carbon monoxide and remaining carbon reduce the iron oxide to iron :

$$Fe_2O_3 + 3\,C \longrightarrow 2\,Fe + 3\,CO$$
$$Fe_2O_3 + 3\,CO \longrightarrow 2\,Fe + 3\,CO_2$$

Simultaneously with the reduction of the ferric oxide, some silica is reduced to silicon, and combines with the iron. The iron also takes sulphur and phosphorus from the ore and coke; and from 2 to 7 % of carbon enters it from the coke. This impure iron settles to the bottom of the furnace, from which place it is drawn off from time to time through a hole, called a tap hole. The stream of white-hot, molten metal is cast into ingots called *pigs* (Fig. 117). The product is known as *pig iron* or *cast iron*. The limestone flux mentioned above combines with the silica and other acidic substances in the ore, and produces the *slag*. Both slag and the molten cast iron collect in the crucible of the furnace, the slag floating on the heavier iron.

FIG. 117. — PIG IRON IN A METAL YARD.

392. The Blast Furnace. — The desirability of cheap and rapid production of cast iron has brought the blast furnace to its present perfection. The opening at the top through which the charging is done is closed by a cup and cone arrangement (Fig. 116). The best modern furnaces have an air lock at the top, closed above and below by a cup and cone. In such a furnace, the charge can be let into the air lock, and then, after the opening at the top is

closed, can be allowed to drop into the furnace. This method prevents the escape of gas during charging. The gases produced during the smelting, which contain about 20% carbon monoxide, are conveyed away from near the

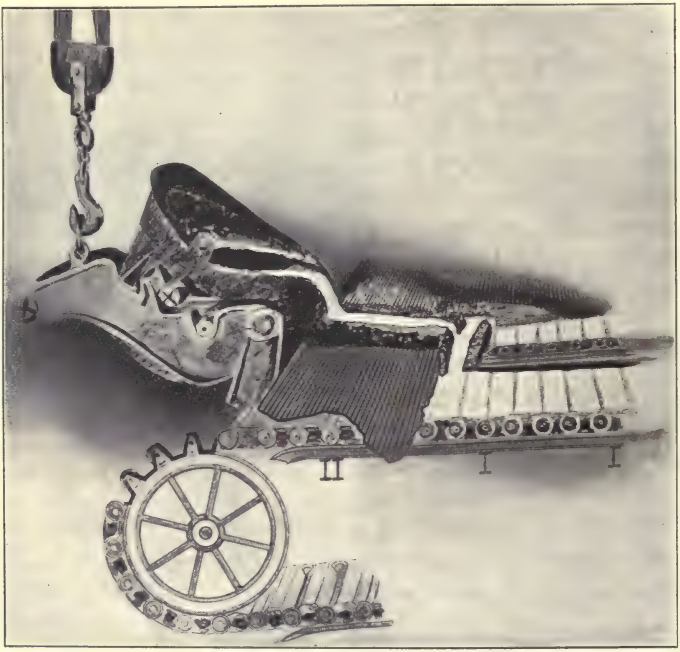


FIG. 118. — CASTING MACHINE, SHOWING METAL RUNNING FROM LADLE INTO MOLDS CARRIED ON AN ENDLESS CHAIN.

top of the furnace through a large flue. This furnace gas is burned to supply heat for the air blast, and under the boilers to generate steam for the engines which compress the air for the tuyères.

The crucible in which the molten iron and slag collect is about 16 feet in diameter. Holes are drilled through its sides for the removal of slag and iron. The process is

called tapping the furnace. As soon as the iron or slag has been removed, the tap hole is closed by a clay plug which is instantly hardened by the heat. The slag is tapped off about every two hours, and the iron every four to six hours. From 80 to 300 tons of metal are drawn off per day. If the iron is to be used in making steel in works near by, it is often carried directly there in large ladles ; otherwise it is run into pigs, which may be cast in sand, or, by means of a casting machine, in iron molds (Fig. 118).

393. Composition and Properties of Cast Iron. — If the iron, after being drawn from the blast furnace, is suddenly cooled, a white cast iron is obtained. The carbon in white cast iron is in chemical combination with the iron as iron carbide, Fe_3C. When the molten iron is cooled slowly, most of the carbon separates in the form of graphite, and the product is known as gray cast iron. As iron carbide is a very hard compound, white cast iron is harder than gray.

Cast iron contains considerable carbon, always over 2% and seldom above 5%. It is the form of iron most easily melted, and expands when it passes from a liquid to a solid state. Therefore, when molten cast iron is poured into a mold, and allowed to solidify, the metal readily takes the shape of the mold. In making castings allowance has to be made for shrinkage, because iron contracts on further cooling after it solidifies. Cast iron is not malleable and can be neither welded nor tempered. It is used for casting articles, such as stoves and ornamental iron work, which are not to be subjected to shock. Wrought iron and steel are made from cast iron. Iron sulphide is generally formed during the smelting of an iron ore and alloys with the iron. Sulphur makes iron "red short" or, in other words, brittle when red hot.

If the ore contains phosphorus, phosphide of iron is formed and dissolves in the iron produced in the blast furnace. Phosphorus makes iron "cold short," that is, brittle when cold. Since both phosphorus and sulphur are harmful to wrought iron and steel, they must be removed when these high-grade products are to be obtained.

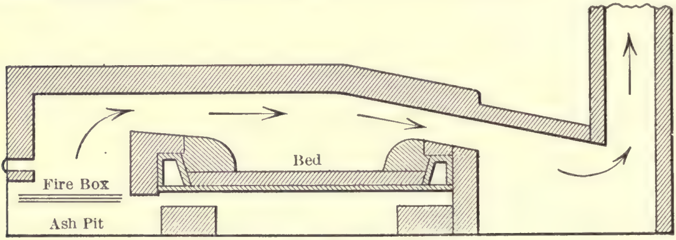


FIG. 119. — REVERBERATORY FURNACE.

394. Manufacture of Wrought Iron. — Wrought iron is made in a reverberatory furnace (Fig. 119) by heating cast iron on a layer of iron oxide. The flames of the burning fuel pass over the furnace charge and the heat reverberates between it and the roof of the furnace. The charge is thus melted without coming in contact with the fuel. Under these circumstances, the greater part of the carbon contained in the cast iron is oxidized to carbon monoxide and passes off. If necessary, a basic lining and a basic slag are used to remove sulphur, phosphorus, and silica from the iron. Basic oxides fuse with the acidic oxides to form salts which enter the slag. The iron becomes pasty, because pure iron has a higher melting point than impure. The molten mass in the furnace is stirred or *puddled* and the pasty iron is gathered into large balls called *blooms*. These are removed from the furnace and nearly freed from slag by a process of squeezing and working under a trip hammer. The iron is then rolled so as to give the product a fibrous

structure, by causing the remaining slag to be distributed through the iron in the form of fine threads. This small portion of slag aids in the process of *welding* iron.

395. Properties and Uses of Wrought Iron. — Wrought iron is the purest form of commercial iron. Good varieties contain not more than 0.3 % of carbon.

When wrought iron is heated, it becomes plastic before melting. When in this condition, two pieces on being hammered together adhere firmly, provided some substance, such as sand, is placed on the iron to dissolve the thin coating of iron oxide that forms on the heated surface. This process is called *welding*. Plastic wrought iron can be hammered into various shapes, rolled into bars, and drawn into wire. Wrought iron is tough and can be bent or stretched without breaking. It can very easily be converted into a temporary magnet. Wrought iron is used to make anchors, chains, wire, and other articles which are intended to withstand sudden and severe strains. As wrought iron can be readily forged and welded, it is the iron used by the blacksmith. It cannot be tempered.

396. Bessemer Steel. — Much cast iron is converted into Bessemer steel, or more properly Bessemer iron. About fifteen tons of molten cast iron are poured into a Bessemer converter (Fig. 120), which is an egg-shaped furnace built of wrought iron plates and lined with a thick layer of refractory material. The bottom is perforated with holes so that streams of air can be blown through the molten metal. The blast lasts from eight to ten minutes, during which time the oxygen of the air unites with the silicon, carbon, and other impurities in the cast iron, leaving nearly pure iron. The heat of combustion raises the temperature of the metal to a high degree, producing what is known as the "boil." Just as the iron commences to burn the blow

is stopped, and the desired amount of a cast iron called *spiegeleisen*, which is rich in carbon and manganese, is added. The blast of air is forced through the mass for a short time to thoroughly mix the ingredients. The spiegeleisen furnishes the desired amount of carbon, and the manganese unites with any dissolved oxygen present. The oxygen is thus prevented from escaping and producing blowholes when the mass cools. The manganese also improves the quality of the metal. At the end of the process, the converter is turned and the contents poured into a ladle and cast.

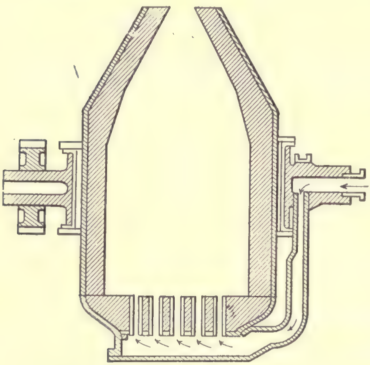


Fig. 120. — Bessemer Converter.

If the pig iron contains sufficient sulphur and phosphorus to materially injure the quality of the Bessemer iron, the converter is lined with basic material. The use of a basic lining was discovered by Thomas and Gilchrist, and the process is named for them. The slag produced, known as Thomas slag, contains basic phosphates and is of value as a fertilizer.

397. Steel by Open Hearth Process. — Much steel is now made by the open hearth process. An open hearth furnace (Fig. 121) has a large bed lined with fire brick and sand on which the charge is placed. By the aid of a *regenerative* heating system, a higher temperature is obtained than would otherwise result. This device is used in many modern furnaces. Gas is used as fuel and is heated before entering the furnace by passing through a checkerwork of hot fire brick. The heated gas is passed into the furnace

through a pipe, while air that has been similarly heated enters through another flue. The burning gas passes over the charge on the furnace bed and the hot, gaseous product escapes through checkerworks which are a duplicate of those used to heat the gas and air. One set of checkerwork is thus raised to a high temperature by the hot

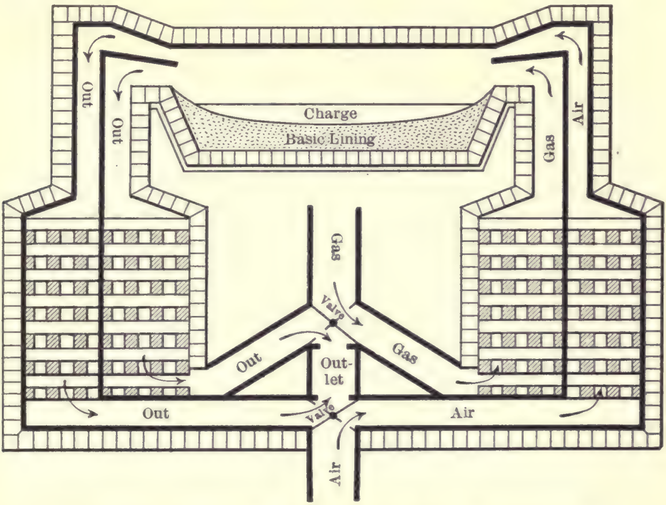


FIG. 121. — OPEN HEARTH FURNACE WITH REGENERATORS.

combustion products, while the other is being cooled as it heats the gas and air about to enter the furnace. About every twenty minutes the direction of the gas and air is reversed by means of a system of valves, so that gas and air pass through the recently heated checkerwork while the flame from the furnace passes through the one just cooled.

The furnace charge consists of scrap steel, pig iron, and iron ore. The scrap steel is placed on the bottom in order to protect it from the oxidizing action of the flame. The manganese and silicon are oxidized by the flame, while

the iron ore is active in furnishing oxygen to consume the carbon. The process consumes from eight to twelve hours and is watched and controlled most carefully by the operator. Samples of metal are repeatedly taken from the furnace and examined to determine when the impurities have been removed and the carbon has been reduced to the desired amount. In case the pig iron contains phosphorus, a basic furnace lining can be used as in the Bessemer process. The steel produced is of much better quality than the metal made by the Bessemer process and is suitable for the manufacture of connecting rods, shafts, armor plate, heavy ordnance, etc., where great strength and ability to stand vibration are required. It can be forged and tempered. The percentage of carbon varies from 0.05 in soft steel to 2.0 in hard.

398. Crucible steel is made in graphite crucibles. The materials used are high-grade wrought iron, scrap steel, and carbon, in the form of hard wood charcoal, coke, or graphite. When pure iron is heated to a temperature above 850°, it is converted into an allotropic form of iron that is capable of absorbing carbon. The carbon at first forms a solid solution with the iron, but after the carbon has reached 0.8 % of the mass, it separates as iron carbide, Fe_3C. Steel always contains iron carbide, which may be either dissolved in the iron, or gathered in particles throughout the mass. In general, the more iron carbide the steel contains the harder it is. In the manufacture of crucible steel (Fig. 122) the iron is melted, a temperature of 1500° C. being maintained for from two to six hours. The heating is continued until sufficient carbon has been absorbed, from the charcoal and the crucible, to make the desired quality of steel. Special crucible steels are made by the addition of various substances to the

crucible charge. Crucible steels are of high grade and are used in making fine edged tools, springs, automobile parts, bridge cables, etc.

399. Special Steels. — Certain of the less familiar metals when added in small quantities produce steels of great hardness, toughness, or tensile strength. More than 8 % of manganese in a steel, or chromium in smaller amount,

Courtesy of the *Crucible Steel Co. of America.*

FIG. 122. — CRUCIBLE MELTING FURNACES.

gives great hardness to the steel. Tungsten and molybdenum are used in making *self-hardening* steels. Tools made from self-hardening steels retain a fine cutting edge without being tempered.

Manganese, chromium, vanadium, and nickel steels are used for safes, armor plates, and parts of machinery subject to great stress or vibration, as shafts or automobile bearings. Deposits of iron ore that had been regarded as too refractory to work have been made valuable by the demand for these special steels.

400. Electric Refining of Steel. — Various types of furnaces are at present used for the refining of steel. Each type has some advantage over the other types. Electric furnaces seem especially adapted to the production of high-grade steels from low-grade materials containing sulphur and phosphorus.

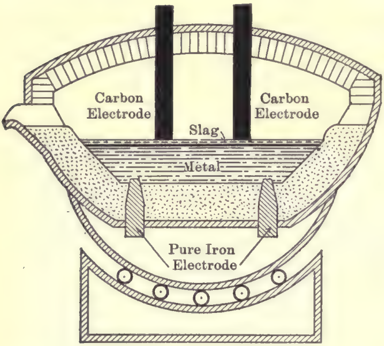


FIG. 123. — GIROD ELECTRIC FURNACE.

Heroult was first to construct a successful arc and resistance furnace for the refining of steel. The Heroult furnace has a capacity up to 15 tons of steel at a charge. Carbon electrodes are used. These cannot come in contact with the iron, since, at the temperature of the furnace, the carbon would rapidly enter into combination with the iron. In the Heroult furnace a basic lining is used and a basic slag covers the steel to be refined. The lower ends of the electrodes dip into the slag on top of the steel to such a depth that the current arcs through the slag to the iron underneath one electrode, passes through the iron to a point beneath another electrode, and then arcs from the iron through the slag to it. The heat generated melts the furnace charge, and sulphur, phosphorus, and other acidic impurities are readily removed by the basic slag.

The Girod furnace (Fig. 123) has upper electrodes made of carbon. These dip into the slag on top of the steel to be refined, as in the case of the Heroult furnace. In the Heroult furnace, the carbon electrodes are widely separated and of different polarity, while in the Girod furnace the carbon rods are near together, and are of the

same polarity. The Girod furnace has also electrodes of soft iron placed at the bottom of the furnace near the outer edge. The carbon electrodes are connected in parallel, so that they are always of the same polarity. The iron electrodes, which are also connected in parallel, have the opposite polarity. The portion of the iron electrodes that extends outside the furnace is water-cooled. The current arcs from the carbon electrodes through the slag to the steel beneath and then passes to the iron electrodes. The charge and chemical action is similar to that in the Heroult furnace. In both furnaces the only effect of the electric current is to develop heat.

401. Tempering of Steel. — The process of varying the hardness of steel by heat treatment is termed *tempering*. As has already been mentioned, all steel contains iron carbide, Fe_3C, a very hard substance that readily dissolves in pure iron at a high temperature (above 670° C.). When all of the iron carbide contained in the steel is in solution and the product is suddenly cooled, further change is prevented, and a steel is obtained that is as hard as it is possible to obtain by heat treatment alone. If a solid solution of iron carbide in pure iron is cooled slowly, a change takes place below 670° C., and the iron carbide gradually passes out of solution and collects in small particles in the iron. We now have a mass of soft iron containing crystals of iron carbide, and the pure iron imparts the property of softness to the mass. The conglomerate of iron and iron carbide is far softer than the solid solution of iron carbide in iron. If a hard steel is heated to a temperature between 430° C. and 670° C., the iron carbide slowly separates from the solid solution and the mass is softened, that is, *tempered* by heat. The amount of iron carbide that separates depends upon the temperature and the length of time used in the heating.

Heating for a long time at moderate temperatures, or quick heating to the higher temperatures below 670° (the temperature at which iron carbide dissolves in iron) accomplishes the same result, viz. the decomposition of the iron carbide. The process, however, can be stopped at any time by a sudden cooling, and a steel of the desired hardness obtained. The temperature can be estimated by a play of colors ranging from yellow to brown, red, purple, violet, and blue, to gray, which appear when the metal is heated. These colors are due to the formation of thin layers of iron oxide, causing interference colors. The colors follow each other when the metal is cooled, and as soon as the right color is obtained the process is stopped by dipping the article into either water or oil.

Color	Temperature	Steel used for
Pale yellow	430°–450°	Razors
Full yellow	470°	Penknives
Brown	490°–510°	Shears and tools for brasswork
Purple	520°	Table knives
Blue	530°–570°	Watch springs and sword blades
Blue-black	610°	Saws and other wood-working tools

The yellow tints give very hard but brittle steels, while, as we proceed toward the blue, the steel is softer but tougher. The films are usually removed by grinding, but are seen on some saws and springs.

402. Classification of Iron and Steel. — Commercial iron is commonly classified as cast iron, wrought iron, and steel. Cast iron contains the highest percentage of carbon, wrought iron the least, and steel usually stands between. Chemical composition, however, is not a sure way of dis-

tinguishing these forms, as some steels contain less carbon than certain wrought irons. Moreover, the condition the carbon is in, whether free or combined with the iron, and whether iron carbide is segregated or is in solution, is as important a factor as its percentage. Knowledge gained from a careful study of the structure of a polished and etched section under a microscope is used as a guide to the true nature of an iron or steel. This, and some recent principles developed by physical chemistry, have put the iron industry on a scientific basis. At best, the classification of iron is difficult, and unless we classify a product according to the process by which it is made, we shall be confused by the many varieties of steel and iron that grade into one another.

COMPARATIVE TABLE OF PROPERTIES

	Cast Iron	Wrought Iron	Steel	
			Low-carbon	High-carbon
Carbon, per cent.	2 % to 7.5 %	0.05 % to 0.3 %	0.05 % to 0.8 %	0.8 % to 2.0 %
Melting point, approximate	1200° C.	1500° C.	1500° C.	1400° C.
Structure	Crystalline	Fibrous	Granular or fibrous	Granular
Hardness	Very hard	Soft	Moderately soft	Hard, if tempered
Possible treatment when heated	Can be cast, but not welded or tempered	Can be welded, but not cast or tempered	Can be cast and welded, but not tempered	Can be cast and tempered. Not easily welded
Uses	Castings, bases and columns	Wire, electro-magnets and malleable iron	Structural steel, wire, nails, sheet	Tools, springs, permanent magnets

SUMMARY

Welding is the process of joining two pieces by heating the surfaces to be joined until they soften, and then causing them to unite by pressure or by hammering.

Tempering is the varying of the hardness of a substance, nearly always steel, by heat treatment. The hardness of steel depends upon the amount of iron carbide the steel contains, and upon whether the iron carbide is segregated or in solution.

EXERCISES

1. Why does not iron occur to any extent in a free state?

2. Why was wrought iron probably the first form of iron worked by man?

3. What becomes of the ashes that would ordinarily result from the combustion of coke when the coke is burned in the blast furnace?

4. Why is it necessary to produce slag in working a blast furnace?

5. What would be the constituents of a furnace charge for smelting an ore consisting of ferrous carbonate mixed with calcium carbonate? Explain.

6. Why cannot wrought iron be tempered?

7. What is the shape of the slag left when wrought iron corrodes? Is the slag left in the same shape when cast iron rusts away?

8. Why does the temperature of the Bessemer converter rise when cold air is blown through the cast iron in it?

9. For what purposes is Bessemer steel inferior to crucible steel? Why?

10. What kind of iron would you use for the manufacture of dynamo cores? Steam radiators? Bridge cables? Anchors? Springs? Chisels? Hammered iron work?

11. Why are the carbon electrodes of an electric furnace used for the refining of steel not permitted to dip into the molten iron?

CHAPTER XXXI

IRON AND ITS COMPOUNDS

403. Pure Iron. — Pure iron may be prepared by the reduction of pure iron compounds, as the oxalate, in a stream of hydrogen; or electrolytic iron may be deposited from solutions of certain iron salts.

Pure iron is a white, lustrous metal which is very tough and which fuses only at a high temperature. It is malleable, ductile, and may be temporarily magnetized.

In dry air, pure iron does not rust, but in moist air rusting proceeds rapidly, particularly if carbon dioxide is present. Iron decomposes water very slowly at ordinary temperatures, but at higher temperatures the reaction proceeds rapidly. With cold, dilute acids, such as hydrochloric and sulphuric, hydrogen is evolved and a ferrous salt is formed. With hot, or more concentrated acids, certain reduction products may be produced. When cast iron is dissolved in acids, the unpleasant odor is due to the formation of hydrocarbons and to sulphur and phosphorus compounds from impurities in the iron.

404. Iron Ions. — Iron forms two kinds of ions, — bivalent, Fe^{++}, and trivalent, Fe^{+++}. Bivalent ions result from the dissociation of ferrous compounds, and trivalent ions from the dissociation of ferric compounds. Compounds in which iron has a valence of *two* are known as *ferrous* compounds; those in which the valence of iron is *three* are termed *ferric* compounds.

405. Oxides of Iron. — *Ferrous oxide*, FeO, can be prepared by the reduction of ferric oxide with hydrogen or carbon monoxide. It is a black powder which cannot be kept in air on account of the ease with which it passes into ferric oxide.

Ferric oxide, Fe_2O_3, forms the most important ore of iron. It can be readily prepared by heating ferric hydroxide, ferrous carbonate, or ferrous sulphide. Ferric oxide constitutes the coloring matter of such pigments as Venetian red, Indian red, and light red. When ferrous sulphate is calcined, a form of ferric oxide known as *rouge* is obtained. Rouge is used for polishing and as a pigment. Limonite, or hydrated ferric oxide ($2\,Fe_2O_3 \cdot 3\,H_2O$), is found in nature mixed with fine clay and sand. Such mixtures constitute the pigment yellow ocher. When calcined, various shades of yellow, orange, and brown are obtained. These are sold as raw sienna, burnt sienna, raw umber, and burnt umber.

The *magnetic oxide of iron*, Fe_3O_4, occurs in nature as lodestone. It is formed when ferric oxide is heated to a high temperature and when iron is burned in oxygen or in air. It constitutes what is known as blacksmith's scale, formed when red-hot iron is worked. When steam is passed over red-hot iron, hydrogen is liberated, and a firmly adhering film of magnetic oxide is deposited on the iron. This film prevents the rusting of the iron under it. *Russia iron*, used as a covering for locomotive boilers, etc., is iron that has been artificially coated with magnetic oxide of iron.

406. Hydroxides of Iron. — *Ferric hydroxide* can be formed by the addition of a base to a solution of a ferric salt:

$$FeCl_3 + 3\,NH_4OH \longrightarrow Fe(OH)_3 + 3\,NH_4Cl$$

It is precipitated as a reddish brown, flocculent compound, which, on drying, changes to iron rust. *Iron rust* may be considered as a double compound of ferric oxide and ferric hydroxide. It is probably produced in a manner analogous to that described for the natural formation of hematite. Iron dissolves either in water or in moisture from the air, that contains carbonic acid, forming acid ferrous carbonate:

$$Fe + 2\,H_2CO_3 \longrightarrow FeH_2(CO_3)_2 + H_2$$

This substance, on drying and further oxidation, is converted into iron rust. If we represent iron rust by the formula $Fe_2O_3 \cdot 2\,Fe(OH)_3$, the chemical equation would be

$$4\,FeH_2(CO_3)_2 + O_2 \longrightarrow Fe_2O_3 \cdot 2\,Fe(OH)_3 + H_2O + 8\,CO_2$$

A coating of rust does not protect the iron under it. The coating does not adhere, but scales off, probably because carbon dioxide, the real cause of rusting, is continually liberated in direct contact with the iron, when the action has once started. Thus iron rust hastens the formation of additional rust.

When ferric hydroxide is heated to a red heat, it is converted into ferric oxide and water:

$$2\,Fe(OH)_3 \longrightarrow Fe_2O_3 + 3\,H_2O$$

Ferrous hydroxide, $Fe(OH)_2$, appears white when first precipitated, but soon changes to dull green and then to brown, by oxidation.

407. Chlorides of Iron. — *Ferrous chloride*, $FeCl_2$, is formed when iron is heated in hydrogen chloride. It is also formed when iron is dissolved in hydrochloric acid in the absence of air. It can be crystallized as a pale green compound, $FeCl_2 \cdot 4\,H_2O$, unstable in air.

Ferric chloride, $FeCl_3$, can be prepared by passing chlo-

rine over hot iron; by dissolving iron in aqua regia; and by dissolving ferric oxide in hydrochloric acid. When hydrogen peroxide is added to a solution of ferrous chloride containing hydrochloric acid, ferric chloride is instantly formed. Ferric chloride is used in medicine, and in general whenever a soluble ferric salt is required.

408. Change of Valence by Oxidation and Reduction. — The changes in valence that take place during certain reactions give an extended meaning to the terms *oxidation* and *reduction*, because such changes in valence are often brought about by the action of oxidizing and reducing agents. Hence the terms *oxidation* and *reduction* are often used to express change in valence. In this sense, *an increase in the valence of the positive part of the molecule is termed oxidation; a decrease in the valence of the positive part of the molecule, reduction.*

The terms are applied to reactions in which oxygen takes no part. If ferric chloride, $FeCl_3$, is treated with nascent hydrogen, ferrous chloride, $FeCl_2$, and hydrochloric acid are produced:

$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$

The iron atom is reduced from a valence of three in the ferric compound to a valence of two in the ferrous compound. By adding nitric acid or some other oxidizing agent to the mixture of ferrous chloride and hydrochloric acid, the ferrous chloride is *oxidized* to ferric chloride, by the addition of an atom of chlorine, thus increasing the valence of the iron:

$$2\,FeCl_2 + 2\,HCl + O \longrightarrow 2\,FeCl_3 + H_2O$$

409. Sulphates of Iron. — *Ferrous sulphate*, $FeSO_4 \cdot 7\,H_2O$, is a by-product in many industries. Scrap iron is added

to sulphuric acid that has been used in the refining of petroleum, or for cleaning iron. The iron is dissolved, and on evaporating the solution, crystals of green vitriol, sometimes called copperas, are obtained. Much ferrous sulphate is used in the manufacture of blue pigments, as a mordant, in the preparation of black inks, and for the precipitation of gold from solutions of its chloride.

When solutions of ferrous sulphate and tannic acid are mixed, ferrous tannate, a nearly colorless compound, is formed. On exposure to the air, ferrous tannate is changed to ferric tannate, which is insoluble, and has a black color. Ferrous tannate is the chief ingredient of iron inks. As the writing would not at first be visible if a solution of pure ferrous tannate were used, some dye is added to give the ink color. On exposure to the air, ferric tannate is formed, which gives the ink its permanent black color.

Ferric sulphate, $Fe_2(SO_4)_3$, is formed when ferrous sulphate is oxidized in the presence of sulphuric acid. It is used with ammonium sulphate in the preparation of ferric ammonium alum, $NH_4Fe(SO_4)_2 \cdot 12\,H_2O$.

410. Ferrocyanides. — On igniting a mixture of nitrogenous organic matter, scrap iron and potassium carbonate, cooling the mass, and then treating it with hot water, *potassium ferrocyanide*, $K_4Fe(CN)_6$, passes into the solution. When the solution cools, crystals of potassium ferrocyanide, or yellow prussiate of potash, separate. These have a composition represented by the formula $K_4Fe(CN)_6 \cdot 3\,H_2O$.

A solution of potassium ferrocyanide does not give the usual characteristic reactions of iron because the iron exists as a part of a complex ion, $Fe\,(CN)_6^{----}$. When solutions of ferric salts and potassium ferrocyanide are

brought together, a deep blue precipitate, ferric ferrocyanide, or Prussian blue, is formed. The reaction is made use of in testing for ferric ions (Fe^{+++}):

$$4\,FeCl_3 + 3\,K_4Fe(CN)_6 \longrightarrow Fe_4[Fe(CN)_6]_3 + 12\,KCl$$

Prussian blue is an important pigment. Bluing, used for laundry purposes, sometimes contains Prussian blue. When the clothes with which it is used are not thoroughly freed from soap, the alkali of the soap decomposes the ferric ferrocyanide, precipitating ferric hydroxide on the cloth and producing spots of iron rust:

$$Fe_4[Fe(CN)_6]_3 + 12\,NaOH \longrightarrow 3\,Na_4Fe(CN)_6 + 4\,Fe(OH)_3$$

411. Ferricyanides. — *Potassium ferricyanide*, or red prussiate of potash, $K_3Fe(CN)_6$, can be prepared by treating a solution of potassium ferrocyanide with chlorine:

$$2\,K_4Fe(CN)_6 + Cl_2 \longrightarrow 2\,KCl + 2\,K_3Fe(CN)_6$$

Solutions of potassium ferricyanide, when added to those of ferrous compounds, give a blue precipitate, ferrous ferricyanide, or Turnbull's blue:

$$3\,FeCl_2 + 2\,K_3Fe(CN)_6 \longrightarrow 6\,KCl + Fe_3[Fe(CN)_6]_2$$

412. Blue Prints, or ferrotypes, the simplest substitutes for the silver photographic papers (§ 436), owe their color to the formation of Turnbull's blue.

When a solution containing ferric chloride and a reducing agent, such as oxalic acid, is exposed to the sunlight, the ferric salt is reduced to a ferrous salt:

$$2\,FeCl_3 + H_2C_2O_4 \longrightarrow 2\,CO_2 + 2\,HCl + 2\,FeCl_2$$

When a sheet of paper is coated in a darkened room with such a mixture, dried and then exposed under a negative to the sunlight, the greatest reduction will take place where the light is brightest. On covering the exposed paper with a solution of potassium ferricyanide, Turnbull's blue will develop wherever ferrous iron exists, and the depth of color will be proportional to the amount of ferrous salt present. In other words, potassium ferricyanide is in this case used as a developer. Where the paper has been protected from the light, the materials are unchanged. The picture can be fixed by washing away the ferric chloride and the excess of potassium ferricyanide.

In making commercial blue-print paper a single compound, ammonium ferric citrate, serves both as the ferric salt and as the reducing agent. The paper is coated with a mixture of this salt and the developer, potassium ferricyanide. Such a paper, after exposure, is both developed and fixed by simply washing with water.

SUMMARY

Pure iron is light gray, malleable, ductile.

Atomic weight 56. Valence 2 or 3. Melting point 1520°.

Iron corrodes when exposed to moist air. Red hot iron decomposes steam. Iron dissolves in dilute hydrochloric and sulphuric acids with the evolution of hydrogen and the formation of a ferrous salt.

Iron forms two **series of salts.** Ferrous salts contain iron having a valence of 2, and ferric salts contain iron with a valence of 3.

The **common oxides** of iron are ferric oxide (Fe_2O_3) and the magnetic oxide of iron (Fe_3O_4).

Ferric oxide pure, or impure and hydrated, is used for several paint pigments.

Russia iron is iron coated with a layer of the magnetic oxide of iron.

Ferric hydroxide is formed when a solution of a base is added to a ferric salt.

Iron rust varies in composition, but may be considered as a double compound of ferric oxide and ferric hydroxide. Iron is prevented from rusting by coating it with paint, enamel, or some metal that does not corrode when exposed to air. Zinc, tin, and nickel are the metals most commonly used for this purpose.

Ferric chloride is the most common ferric salt.

Ferrous sulphate, green vitriol, is the most common ferrous salt. It is used in the manufacture of inks and paint pigments.

Yellow prussiate of potash is potassium ferrocyanide, $K_4Fe(CN)_6$.

Red prussiate of potash is potassium ferricyanide, $K_3Fe(CN)_6$.

Blue prints are made on paper coated with a ferric salt, potassium ferricyanide, and a reducing agent.

An increase in the valence of the positive part of the molecule is sometimes termed **oxidation**.

A decrease in the valence of the positive part of the molecule is sometimes termed **reduction**.

EXERCISES

1. Which would have the higher melting point, pure iron or ordinary wrought iron? What principle is illustrated by these melting points?

2. Is pure hydrogen formed when hydrochloric acid is added to cast iron? Explain.

3. Is ferrous sulphate, or ferric sulphate, formed when iron is treated with an excess of sulphuric acid?

4. How would you convert ferrous chloride into ferric chloride? Ferric chloride into ferrous chloride?

5. How would you determine whether a solution contained a ferric or a ferrous salt?

6. What chemical change takes place when ferrous sulphate is calcined? Mention important uses of the chemical compound that constitutes the residue.

7. Why is it difficult to keep a solution of ferrous chloride?

8. Which oxide of iron is used as a protective coating for iron? Which one accelerates the rusting of iron?

9. Briefly state the important changes that take place during the making of a blue print.

10. Give two definitions for oxidation. For reduction.

11. Which is involved in the conversion of ferrous sulphate into ferric sulphate, oxidation or reduction? In the conversion of potassium ferrocyanide into potassium ferricyanide?

12. Name an acid suitable for removing iron rust spots from cotton cloth.

13. Why does the color of an iron ink change on exposure to air?

CHAPTER XXXII

COPPER AND ITS COMPOUNDS

413. Occurrence and Ores. — Copper is the only metal which occurs free in large, widely distributed deposits. For this reason, it was the first metal extensively used by man. The copper age followed the stone age. The island of Cyprus was noted in the time of the Romans for its production of copper or Cyprian brass. We obtain the symbol Cu from the Latin name, *cuprum*.

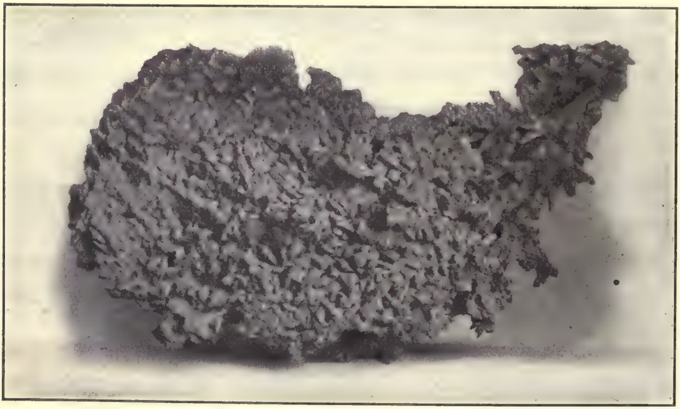


FIG. 124.— MASS OF NATIVE COPPER (3 x 2 ft.) IN THE UNIVERSITY OF MICHIGAN MUSEUM.

The noted mines of native copper in Michigan, along the southern shore of Lake Superior, were extensively worked before Columbus discovered America. From them masses of copper of enormous size, one of which

weighed nearly five hundred tons, were obtained. These mines are still an important source of copper.

The ores of copper are numerous, and many of them have a composition represented by complex formulas; the more important ores besides native copper are sulphides, oxides, carbonates, and silicates. Much copper is obtained from an ore named chalcopyrite, the composition of which corresponds approximately to the formula $Cu_2S \cdot Fe_2S_3$. Malachite, a basic carbonate of copper, $CuCO_3 \cdot Cu(OH)_2$, is of interest. Polished slabs of malachite often exhibit variegated patterns of different shades of green which are of great beauty, and the mineral is highly valued for ornamental purposes.

414. Metallurgy; Steps in Process. — The metallurgy of copper is usually complex; not only does the process vary with the kind of ore used, but similar ores, in different localities, are seldom treated in the same manner. In case the ore contains much chalcopyrite, the process, as carried out by one of the large copper companies, consists essentially in:

1. Roasting a *portion* of the ore to remove sulphur.
2. The production of a complex sulphide called *matte*.
3. Converting the matte into blister copper.
4. Poling the blister copper and casting it into anode plates.
5. Refining by electrolysis.

415. Roasting of Ore and Production of Matte. — When chalcopyrite, $Cu_2S \cdot Fe_2S_3$, is roasted, the following reactions probably take place:

$$Fe_2S_3 + 4\,O_2 \longrightarrow 2\,FeO + 3\,SO_2$$
$$2\,Cu_2S + 3\,O_2 \longrightarrow 2\,Cu_2O + 2\,SO_2$$

The roasted ore is then smelted for the production of matte, in a blast furnace, similar in construction to the iron blast furnace (§ 392). The charge for the furnace consists of the roasted ore, a certain amount of unroasted (green) ore, and coke. The ores usually contain considerable silica, which plays an important part in the action.

The copper oxide of the roasted ore reacts in the furnace with the iron sulphide of the unroasted ore:

$$3\,Cu_2O + Fe_2S_3 \longrightarrow 3\,Cu_2S + Fe_2O_3$$

As copper has a greater tendency to combine with sulphur than has any other metal present, all the copper is changed to sulphide. A part of the iron oxidizes and unites with the silica which is present in the ore and forms a fusible glassy slag. Some of the iron sulphide remains with the cuprous sulphide, forming the *matte*, which is a more or less pure mixture of cuprous and ferrous sulphides. In addition to the sulphides mentioned, matte contains all of the gold and silver present in the ore, and generally arsenic and antimony.

The matte and slag are run into a shallow tank called a forehearth, where the lighter slag rises to the top and overflows through a trough, while the matte collects at the bottom and is from time to time drawn off through a pipe. Matte contains from 45% to 60% of copper.

416. Conversion of Matte to Blister Copper. — Matte is converted into blister copper by Bessemerizing, in a furnace somewhat similar to that used for the production of Bessemer steel (Fig. 120). The matte is melted and poured into the converter; then air is blown through the molten mass (Fig. 125). Sulphur, iron, and other impurities are oxidized. Those oxides which are volatile are driven off. The iron oxide, however, unites with the

quartz of the furnace lining to form a slag. The copper obtained still contains all of the gold and silver present in the original ore, and small quantities of other impurities. Molten copper dissolves considerable sulphur dioxide, which is expelled when the mass cools, giving the copper the appearance which causes it to be called *blister copper.*

By courtesy of *The Scientific American.*

FIG. 125. — CONVERTER IN OPERATION.

The matte is often converted to blister copper by heating and melting it in a reverberatory furnace similar to that used in the next operation, and allowing the sulphur to be oxidized by the air passing over it.

417. Poling of Blister Copper and casting of Anode Plates. — Blister copper is melted in a reverberatory furnace

FIG. 126. — REVERBERATORY FURNACE FOR POLING COPPER.

(Fig. 126), and the molten mass is stirred and reduced by the gases coming from a long pole or log of green wood, which is forced into the metal. The hydrocarbons distilled from the wood unite with the oxygen combined with the copper. This process, called *poling*, has for its object the reduction of the small amount of copper oxide that is present to metallic copper. Any one who has seen the interior of a poling furnace in operation will retain a vivid impression of the seething mass of molten copper, dazzling in its brilliancy of color. After being poled, the copper is cast into anode plates to be refined by electrolysis.

By courtesy of *The Scie tific Americ n.*

FIG. 127. — TANK-HOUSE FOR ELECTROLYTIC COPPER REFINING.

418. Refining by Electrolysis. — The anode plates from the poling furnace are about $\frac{3}{4}$ of an inch thick, 3 feet wide, and 3 feet long. The cathode plates are of pure copper about $\frac{3}{16}$ of an inch thick. They are suspended

in wooden tanks containing a warm solution of copper sulphate acidulated with sulphuric acid (Fig. 127). During the electrolysis the solution is kept slowly circulating, and at a definite concentration. When the current passes, pure copper is deposited on the cathode. A part of the impurities enter the bath, while others, including gold and silver, fall to the bottom of the tank and form a substance known as *mud*. The gold and silver are recovered from the mud.

The cathode plates for this process are made at the refinery. Some copper refiners do not use pure copper cathode plates, but arrange the impure plates so that the copper from the front of one plate is deposited on the back of the next one.

419. Properties of Copper. — Copper has a characteristic reddish color. Only two of the common metals, gold and silver, surpass it in malleability and ductility. It stands next to silver as a conductor of electricity.

On exposure to the atmosphere, copper is attacked by carbon dioxide in the presence of moisture, and becomes covered with a coating of a basic carbonate of a greenish color. The coating, once formed, adheres to the copper underneath and protects it. Copper is readily attacked by nitric acid (preparation of nitric oxide, § 249), but neither dilute hydrochloric acid nor dilute sulphuric acid attack it in the absence of air. It is readily acted upon by hot, concentrated sulphuric acid (preparation of sulphur dioxide, § 206). Boiling concentrated hydrochloric acid slowly converts copper into cuprous chloride, $CuCl$.

420. Uses of Copper. — Large quantities of copper are used for a great variety of purposes. Among the more important may be mentioned its use as wire and cables

for the transmission of electric currents; for this purpose it must be practically pure, as very small amounts of impurity considerably impair the conductivity. If the conductivity of pure copper is considered as 100, copper containing 0.8 % of arsenic has a conductivity of only 30, and copper containing 0.5 % of silicon has a conductivity of 28. Other uses of copper include its employment in the manufacture of various articles for domestic and scientific purposes, such as water heaters, kettles, stills, vacuum pans, etc. Much copper is also employed in the manufacture of alloys. *Brass* is an alloy of copper and zinc; *bronze* is an alloy of copper and tin, to which sometimes zinc and other metals are also added; *German silver* is an alloy of copper, nickel, and zinc; and *aluminum bronze* is an alloy of copper and aluminum.

421. Compounds of Copper. — Copper forms two kinds of ions, cuprous, Cu^+, and cupric, Cu^{++}. Its valence may therefore be considered to be sometimes one and at other times two. The univalent cuprous ion unites with negative ions to form cuprous compounds, while the divalent cupric ion forms cupric compounds.

	Oxide	Sulphide	Chloride
Cuprous	Cu_2O	Cu_2S	$CuCl$
Cupric	CuO	CuS	$CuCl_2$

422. Oxides of Copper. — *Cuprous oxide*, or red oxide of copper, Cu_2O, occurs in nature. When a strip of copper is heated in air, a layer of cuprous oxide may be found under the layer of black cupric oxide. If a mixture of cupric oxide and charcoal is heated, the cupric oxide is first reduced to cuprous oxide, and then the cuprous oxide is reduced to copper. Other reducing agents have a

similar effect on cupric oxide. The formation of cuprous oxide is utilized in testing for glucose by means of Fehling's solution. Fehling's solution contains cupric sulphate, potassium hydroxide, and Rochelle salt. When it is added to a solution containing glucose, or a similar reducing agent, and the mixture is boiled, cuprous oxide separates as a red precipitate. The Rochelle salt is added to prevent the formation of cupric oxide, which, being black, would hide the color of the cuprous oxide. Cuprous oxide is used to give a beautiful red color to pottery.

Cupric oxide, or black oxide of copper, CuO, can be prepared by heating copper in air and also by heating cupric hydroxide, nitrate, or carbonate. Many compounds containing hydrogen are oxidized when heated with cupric oxide, the hydrogen being converted into water. If carbon is present, it is converted into carbon dioxide. These facts make cupric oxide a valuable substance to use in the determination of the quantity of hydrogen and of carbon present in compounds containing these elements.

423. Preparation of Copper Sulphate. — Crystallized copper sulphate, or blue vitriol, $CuSO_4 \cdot 5\ H_2O$, is prepared on a large scale by placing coarse copper shot in a perforated lead basket, and then causing the basket and contents to move up and down so that they will at one time be in the air and at another time immersed in warm, dilute sulphuric acid. When the basket enters the acid, air is carried into the acid with the shot. The action of the acid on the copper in the presence of air results in the formation of copper sulphate, which passes into solution:

$$2\ Cu + O_2 + 2\ H_2SO_4 \longrightarrow 2\ CuSO_4 + 2\ H_2O$$

The solution, after being sufficiently concentrated, is allowed to stand in lead-lined vats in which are suspended

lead strips. Blue vitriol crystallizes on the lead and is purified by recrystallization.

Blue vitriol is also obtained as a by-product in one method used in separating gold from silver. The melted alloy of these two metals is granulated by pouring it into cold water. The granulated mass is boiled with concentrated sulphuric acid until the silver is dissolved as silver sulphate. The gold remains undissolved and settles to the bottom of the vat. The solution of silver sulphate is removed to lead-lined vats and the silver separated by the addition of copper:

$$Ag_2SO_4 + Cu \longrightarrow CuSO_4 + 2\ Ag$$

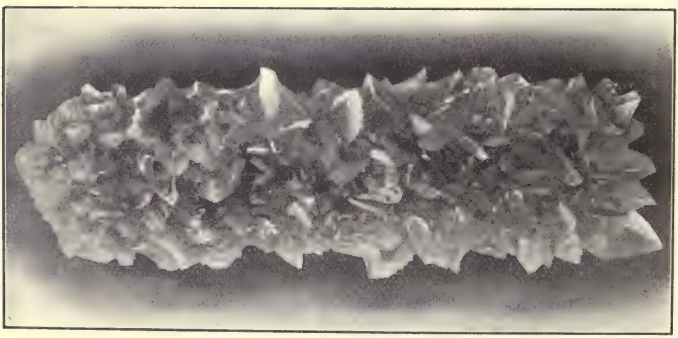


FIG. 128. — COPPER SULPHATE CRYSTALS.

424. Properties and Uses of Copper Sulphate. — Copper sulphate forms deep blue crystals (Fig. 128) which effloresce in dry air. Its water solution gives an acid reaction with litmus (§ 183).

For some time the great value of copper sulphate as a fungicide has been recognized. A mixture of copper sulphate and slaked lime, known as the Bordeaux mixture, is now extensively employed for this purpose. A thick paste of calcium hydroxide and copper sulphate was first

used near the city of Médoc, France, to keep boys from stealing grapes. When placed upon the trellises and vines it was conspicuous, and was believed to be poisonous. In 1882, Millardet, professor of botany in Bordeaux, visited the vineyards near Médoc, and was informed by the grape growers that those portions of the vineyard which had been treated with the paste were not attacked with mildew. Much work has been done in the United States Department of Agriculture in determining the value of the Bordeaux mixture as a general fungicide. Its use in this country has saved crops worth many thousands of dollars.

Dilute solutions of copper sulphate are used to moisten seeds of cereals prior to sowing, to prevent the attack of fungi called smuts.

Plants known as algæ grow abundantly in the water of ponds and reservoirs. Some of them impart to the water disagreeable odors; others produce effects equally undesirable. Copper sulphate is added to the water of ponds thus affected, in the proportion of one part of copper sulphate to from one to eight million parts of water, for the purpose of destroying algæ. The solution is too dilute to kill fish. The copper sulphate appears to react with the albumen of the algæ to form an insoluble substance which sinks to the bottom of the ponds.

Copper sulphate has many other important uses. It is employed in batteries, in electroplating, as a mordant in dyeing, and for making other compounds of copper.

SUMMARY

The atomic weight of copper is 63.6. Specific gravity 8.9. Melting point 1083° C.

Copper occurs as metal; this and the sulphides are its principal sources.

It is separated from its ores by burning out the sulphur and reducing the oxide by carbon. It is purified by electrolysis.

Copper is durable under ordinary atmospheric conditions, and is used for protective coverings. Being ductile and a good conductor, it is used for electric conductors. As a constituent of many alloys, copper finds wide use.

Copper sulphate is the most important compound of copper. It is used as a fungicide, for paints, for plating, and in some batteries.

EXERCISES

1. What metals are usually found associated with copper?

2. How is iron separated from copper? How is silver?

3. Heavy electric cables of copper often have iron wire above them to which they are fastened. Why?

4. What is the result of the action of atmospheric agents on copper?

5. What volume of nitric oxide will be produced by the action of 10 grams of copper with nitric acid?

6. How could you tell whether a given substance was gilt (brass) or gold?

7. What is the most important use of copper? How does its purity affect its fitness for this purpose?

8. Name three alloys of copper and their constituents.

9. What copper compound is used in pottery and in glass? Why?

10. What would be obtained if ammonia were passed over heated copper oxide?

11. How much blue vitriol could be obtained, using one ounce of copper?

12. Write the equation for the change that takes place when a strip of copper is placed in a solution of silver nitrate.

13. How much copper could be obtained from one ounce of blue vitriol?

14. One gram of silver is obtained by the decomposition of its sulphate by copper. What weight of copper passes into solution?

15. Calculate the percentage of water of crystallization in crystalline copper sulphate, $CuSO_4 \cdot 5\ H_2O$.

16. State two uses for copper sulphate.

17. How could you tell whether or not a given substance is a compound of copper?

18. Outline the process by which a vessel might be copper plated.

CHAPTER XXXIII

SILVER, GOLD, AND PLATINUM

SILVER

425. Occurrence. — Silver is the most common of the precious metals. Silver has been known from the earliest times, as it frequently occurs free in rocks and is easily separated.

Native silver is found in Arizona, Mexico, South America, and elsewhere, but much of the silver now used is obtained from sulphide ores, usually associated with lead, copper, arsenic, and gold. Silver chloride (horn silver) occurs in nature, and traces of silver compounds are found in sea water. The principal supply of silver is from Mexico, United States, Canada, Australia, and Peru.

426. Metallurgy. — Some of the ores of silver are so complex that various processes are employed in the separation of the metal, but since so large a proportion of the commercial metal is obtained from lead ores, only the method used for these (Parkes' process) will be described.

The ore, largely lead sulphide, is roasted to remove sulphur, and then reduced as described under the metallurgy of lead (§ 471). The crude metal thus obtained is heated in a reverberatory furnace and stirred. Such metals as copper, antimony, and arsenic are oxidized, forming a scum on the surface of the lead, and this is skimmed off. The molten metal is now run into iron pots and a small percentage of zinc is stirred into it. As the

mixture cools, an alloy of zinc with silver and gold comes to the top and is skimmed off, but little of the lead being removed. If there is much silver in the crude lead, the treatment with zinc may be repeated.

The skimmings containing zinc, lead, silver, and gold are now heated in a retort and the zinc removed by distillation.

The residue, containing lead, silver, and gold, is then *cupelled*, that is, heated in a bone-ash dish in a shallow furnace exposed to the air. The lead oxidizes, and the melted lead oxide flows off and is recovered. The melted silver and gold that remains is then poured into molds. A small cupellation furnace is shown in Fig. 129; *a* is a muffle and *b* the cupel in which the silver and gold is finally left as a metallic button.

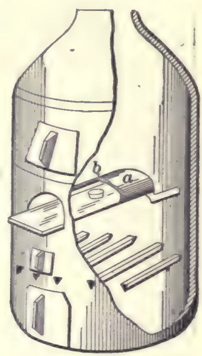


FIG. 129.

The gold is separated from the silver by treating the alloy with hot concentrated sulphuric acid or nitric acid. The silver dissolves as the sulphate or the nitrate, but the gold is not affected, and after washing is melted and cast into bars.

The silver is recovered from the solution by hanging in it plates of copper:

$$2\,AgNO_3 + Cu \longrightarrow Cu(NO_3)_2 + 2\,Ag$$

The silver is deposited in a fine crystalline form known as *cement silver*. The "silver tree" (Fig. 130) is produced in this way.

Another method of separating gold from silver is by electrolysis. The alloy is made the anode in a dilute nitric acid solution of silver nitrate, the anode sheet being inclosed in a canvas bag. With a current of low voltage,

silver is dissolved from the anode as the nitrate and redeposited on the cathode as practically pure metal. The gold is unaffected and remains at the anode, and as the anode disintegrates, collects as a mud in the canvas bag.

427. Physical Properties. — Silver is a white metal, fairly hard, capable of receiving and retaining a high polish. It is the best conductor of heat and of electricity. Being ductile and malleable, it is readily worked into articles of various shapes.

FIG. 130. — SILVER TREE.

428. Chemical Properties. — Silver does not change in pure air and does not oxidize on being heated. It darkens readily in the presence of sulphur compounds, showing such stains as are seen on silver spoons that have been used with eggs or mustard, on coins carried in the pocket, or on silverware about the house. "Oxidized" silver owes its color to a thin coating of silver sulphide, produced by dipping the metal in a solution of crude potassium sulphide.

Alkalies do not affect silver. Nitric and sulphuric acids react with it as they do with copper:

$$2\,Ag + 2\,H_2SO_4 \longrightarrow Ag_2SO_4 + 2\,H_2O + SO_2$$
$$3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + 2\,H_2O + NO$$

429. Cleaning Silverware. — The tarnish may be removed from silver by rubbing with a very fine abrasive, like diatomaceous earth (electrosilicon), or by dissolving it

chemically. Moistening a dry silver polish with ammonia aids its action, on account of the solvent power of the ammonia. The cyanide solution used by jewelers should never be employed in the home, as it is one of the most deadly poisons known.

Recently a simple and very satisfactory method of cleaning silverware by boiling it with water in an aluminum dish, has been devised. In this case, aluminum replaces the silver in the compounds forming the tarnish. In cleaning plated silver, the fact that the plating is pure silver and is, therefore, softer than ordinary sterling or coin silver should be kept in mind. Plated silver should never be rubbed hard with abrasive polishes, even those which might be suitable for solid silver.

430. Uses of Silver. — Since pure silver is not hard enough to stand the wear and tear of constant use, it is alloyed with other metals, for instance copper. The silver coins of the United States contain 90% of silver and are said to be 900 fine. British coins are 925 fine (92.5% silver), and this is the grade known as *sterling silver*. On account of its color, durability, and luster silver has long been used for jewelry and ornaments, and as a plating on cheaper metals.

Mirrors are made by depositing a layer of silver on polished glass. A solution of silver nitrate to which has been added some ammonia and a reducing agent, as formaldehyde or grape sugar, is flowed over the glass and gently warmed. The silver is reduced and deposited as a bright film on the glass. This is washed, dried, and varnished to protect it.

431. Silver Plating is usually done by electrolysis. To secure a firm, uniform deposit, the electrolyte is a solution

of silver and potassium cyanides (Fig. 131, *b*) made by adding potassium cyanide solution to a solution of silver nitrate until the precipitated silver cyanide is dissolved. A bar or sheet of silver is used as the anode (*a*) and the object to be plated as the cathode (*c*), a rather weak current being employed. The positive silver ions are discharged and deposited on the cathode. The negative cyanide ions, discharged on the anode, combine with the silver, forming silver cyanide. This, on dissolving, is dissociated. The amount of silver in the solution is unchanged, for silver is dissolved from the anode and deposited on the cathode.

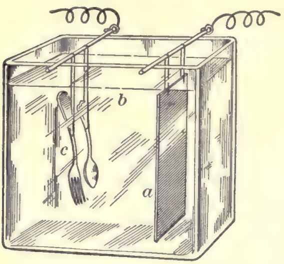


FIG. 131. — SILVER PLATING.

432. Compounds of Silver. — *Silver nitrate*, $AgNO_3$, is the most common compound. It is prepared by dissolving silver in nitric acid:

$$3\,Ag + 4\,HNO_3 \longrightarrow 3\,AgNO_3 + 2\,H_2O + NO$$

It is very soluble in water and crystallizes from it in flat, rhomboidal, transparent crystals. In contact with organic matter and exposed to the light, it darkens. Molded into sticks, silver nitrate is used as a cauterizing agent for warts, wounds, and sores, and is known as *lunar caustic*. Silver nitrate is the most important compound of silver because most of the other silver compounds are made from it.

Silver chloride, AgCl, is made by adding a solution of a chloride to a solution of a silver salt:

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3$$

The silver chloride separates as a white, curdy, insoluble solid. Silver chloride does not dissolve in acids, but dissolves in ammonia and in sodium thiosulphate, the *hypo* of the photographer.

Silver bromide, AgBr, and *silver iodide*, AgI, resemble the chloride; they have a yellowish tinge, are more easily changed in the light, and are less soluble. Like the chloride, they are extensively used in photography.

PHOTOGRAPHY

The preparation of the photographic negative involves these processes: the exposure, the development, the fixing, and the washing.

433. Exposure. — The photographic plate consists of glass or transparent celluloid coated with a film of gelatine containing very finely divided silver bromide, which, as has been stated, is *sensitive* to light in that it becomes somewhat less soluble and *more easily reduced.* In the camera the plate is exposed to light, and the change in the silver bromide is produced, strongly where the light is bright, less intensely in the shadows. The exposure is very short in the camera, and produces no *visible* change in the plate.

434. Developing. — The next operation is to develop the picture. As the exposed silver compound is a little more easily affected than the unexposed compound, it is possible to change the one without materially affecting the other. For this, the *developer* is used. *The developer is a reducing agent of such strength that it is capable of continuing the change begun by the light, but is not capable of initiating the change in the unaffected parts of the plate.*

Ferrous sulphate, pyrogallol, hydroquinone, and many other reducing agents are used as developers.

$$2\,AgBr + H_2O \longrightarrow 2\,Ag + 2\,HBr + O$$

The acid is neutralized by the alkali added in the developer, and the oxygen is removed by the reducing agent. Where the plate has been exposed to the light, there will be a deposit of silver, which appears dark because it is very finely divided. Where no light acted, the silver compound is unchanged.

435. Fixing. — When it is seen that the picture is developed sufficiently, it is placed in the *fixing bath.* This is a solution of sodium thiosulphate, $Na_2S_2O_3$, commonly called hyposulphite of soda, and is capable of dissolving many silver *compounds*, such as the silver bromide, which remains unreduced in those parts of the picture where the light has acted least. This unchanged silver bromide is dissolved, and the glass remains *clear* in these places. As all the material sensitive to light has been removed, the plate is said to be *fixed;* it is then thoroughly washed and dried.

On the fixed plate, those parts of the scene which are brightest, that is, those parts which are white or blue, are represented by a dark deposit of silver; the dark parts of the scene are clear, so that shades are reversed; hence it is called a *negative* (Fig. 132, *b*).

436. Printing and Toning. — The finished picture on paper is made from the negative. The paper is *sensitized*, as was the plate, by a film of silver chloride or bromide. It is exposed to the light under the negative. Now those parts of the paper under the clear parts of the negative will be affected most by the light and will be the darkest

on reduction; the parts under the heavy deposits will be little affected and appear light, as they do in the object, so that the print, being the reverse of the negative, is a *positive* (Fig. 132, *a*). Its shades agree with those of the object.

The positive is developed in the same manner as the negative in most cases, but in *printing out* papers, the developer is in the paper, so that the reduction occurs

a, Positive.

b, Negative.

Fig. 132.

and the picture appears during the exposure. The print is fixed and washed as the plate was, and to render it more permanent and to improve the color, the print is *toned* by immersing it in a solution of gold chloride, so that some of the silver of which the picture is composed is replaced by gold, giving it a warmer tone. Platinum and lead compounds are also used in *toning*. A tintype is a whitened negative on a polished black surface. Other materials might be used besides silver compounds, but these are the most sensitive to slight variations in light

and are the most easily controlled. The blue print process is described in § 412.

GOLD

437. Occurrence. — Gold has been known from the earliest times. At present the principal supply comes from Africa, the United States, and Australia. It commonly occurs native, or alloyed with silver and other metals. It also occurs combined with tellurium, an element closely related to sulphur. Native gold is found in veins running through quartz rock and also in the beds of streams whose sands have been formed from the disintegration of such gold-bearing quartz. It often occurs in nuggets varying in size from that of a tiny pebble to a mass weighing over a hundred pounds.

438. Separation. — From river sands and gravel gold is separated by washing with water. The lighter rock particles are washed off, leaving the gold. Partially disintegrated rock and coarse gravels are sometimes mined by dredging, crushing and washing them with streams of water through troughs, with transverse cleats holding mercury along the bottom. These retain the heavy gold and permit the soil and gravel to be swept on.

439. Metallurgy. — When gold occurs in veins in massive rock, the rock is blasted with dynamite. The broken rock is crushed to small pieces by powerful iron crushers and is then pounded into fine powder by heavy iron stamps working in iron troughs. Water is kept flowing through these troughs, and the gold and rock leave them as a thin mud. This is caused to flow over silver-plated copper plates coated with mercury. The mercury amalgamates with the gold, and when a sufficient quantity

accumulates, the amalgam is scraped off the plates and freed from mercury by distillation.

The gold that escapes amalgamation is extracted by means of sodium cyanide. The mud is allowed to stand in a weak solution of cyanide exposed to air for days or weeks and a double cyanide of gold and sodium is formed. The gold is precipitated from this solution by zinc or is extracted by electrolysis. This cyanide process is also applied directly to ores poor in gold and to tellurides. Its use in this country is increasing.

The separation of gold from copper slimes has already been mentioned (§ 418).

440. Properties. — Gold is soft and heavy and is the most malleable and ductile of metals. The presence of a small amount of other metals, however, often makes it brittle. Gold leaf has been made $\frac{1}{250000}$ of an inch thick. Gold leaf transmits green light, while finely divided gold, when suspended in liquids, appears purple by reflected light, and blue by transmitted light. Gold in this form is known as *colloidal* gold.

Gold is unaffected by air or water at any temperature. Ordinary acids do not act on it, but it is dissolved by *aqua regia*, with the formation of auric chloride, $AuCl_3$.

441. Uses. — Pure gold is used as gold leaf. The metal is too soft to be used alone for other purposes and is alloyed with silver or copper. The proportion of gold is always indicated by the number of carats fineness: pure gold is 24 carats fine, 18-carat gold contains 18 parts by weight of gold and 6 parts of other metal. This carat should be distinguished from the carat used in weighing gems, which has recently been standardized at a weight of 200 milligrams. The gold coins of the United States are

90 % gold and 10 % copper. Articles are gold plated by an electroplating process with a bath of double cyanide of gold and potassium.

COLLOIDS

442. Nature. — The finely divided gold mentioned in § 440 is an example of a large class of substances known as *colloids.* Colloids form suspensions with liquids, in which the colloid is as uniformly distributed through the liquid as a dissolved substance is in its solvent. These colloidal suspensions can often be filtered without change and the colloids do not settle out of the suspension on standing. Ordinary soluble substances, such as the soluble acids, bases, and salts, are sometimes called *crystalloids*, as most of them form crystals when the water in which they are dissolved is evaporated. If a mixture of a crystalloid solution and a colloidal suspension be placed in an animal or vegetable membrane and immersed in running water, the crystalloid will eventually be all washed out, while the colloid will not leave the membranous bag. Such a membrane is called a *dialyzing membrane.* In a solution of a crystalloid, we have assumed that the crystalloid was divided into particles usually smaller than the molecules (§ 148); such particles will pass through a dialyzing membrane. Evidently the particles of a colloid are much larger, as they cannot pass through the pores of such a membrane. *A colloid, then, is a substance which forms uniform permanent suspensions with liquids, and whose particles cannot pass through a dialyzing membrane.* Colloids affect very little the boiling point and the freezing point of the liquid in which they are suspended.

443. Production. — Colloids are produced in a number of ways. Colloidal gold, silver, copper, or platinum may be

obtained by establishing an electric arc between wires of one of these metals beneath the surface of very pure water. They may also be obtained by chemical reactions carried out under very restricted conditions. These colloidal suspensions of metals show a considerable variety of color, according to the conditions under which they are prepared.

444. Importance. — The practical importance of colloids is enormous. A great number of common substances, such as gelatine, glue, starch, leather, paper, and rubber, are natural or artificial colloids. Fertile soil must be largely in a colloidal condition in order that moisture and the nutriment from fertilizing material may be *adsorbed*, that is, condensed on the surface of its particles. The cell walls of the tissues of the body are dialyzing membranes, through which colloids cannot pass, and the processes of nutrition largely depend upon the formation of colloids at the right time and place. Glass is colored by making colloidal suspensions of metals in the melted glass; ruby glass is colored with colloidal gold.

PLATINUM

445. Occurrence. — Platinum occurs native, alloyed with osmium and iridium, which closely resemble it, and with other metals. The most important deposits of platinum are in the Ural Mountains; it is also found in California, Australia, and a few other places. The separation of platinum from the metals alloyed with it is a complicated process.

446. Properties. — Platinum is a white, lustrous metal, about twice as heavy as lead. It is very malleable and ductile and is infusible except in the oxyhydrogen flame or the electric arc. The metal is permeated by or *occludes*

large quantities of hydrogen when cold, with an increase in temperature, and releases the hydrogen when ignited. It does not take up oxygen when hot, but condenses it on the surface when cold. Platinum may be obtained as a fine black powder, *platinum black*, by the action of a reducing agent on a solution of one of its salts and as a *spongy platinum* by igniting the double chloride of platinum and ammonium. When platinum is to be used as a catalytic agent, these forms produce a maximum effect for the money invested, on account of the large surface they possess in proportion to their mass.

Platinum is not attacked by air or water at any temperature, and is not affected by acids, except *aqua regia.* Caustic alkalies, phosphorus, silicon, and carbon attack it when hot, so none of these substances should be heated in platinum vessels. Platinum should never be heated in a smoky flame, on account of its tendency to form a carbide, nor should metals be heated in platinum vessels.

447. Uses. — The infusibility of platinum and its chemical indifference toward the great majority of elements and compounds render it invaluable in chemical operations. It finds extensive use in the laboratory, in the form of dishes, wire, and foil. On account of its cost, which is more than that of gold, it is used only to a limited extent in chemical manufactures. The great expense, however, is partly compensated for by its indestructibility. It is used for pans for the concentration of sulphuric acid, and large quantities of platinum black are employed as a catalytic agent in the manufacture of sulphuric acid by the contact process. It is a good conductor of electricity and expands with heat at the same rate as glass. On account of these properties it is sometimes used to connect the filaments of incandescent lamps with the wires out-

side the bulbs. The power of platinum to cause the ignition of inflammable gases mixed with air is utilized in self-lighting burners and mantles. Its alloy with iridium is hard and unalterable in air and is used for the manufacture of government standards of length. A considerable amount of platinum is used in settings for jewels. This is unfortunate, as much platinum needed for industrial operations is thus withdrawn from the market.

448. Compounds of Platinum. — The most important platinum compound is *chlorplatinic acid*, H_2PtCl_6, which is formed by dissolving platinum in *aqua regia*. This forms chlorplatinates with metallic compounds. It is used in toning platinum photographs and as a test for potassium compounds. The test depends upon the fact that potassium chlorplatinate is but slightly soluble in water or alcohol, while the corresponding sodium compound is decidedly soluble.

SUMMARY

Silver occurs native, and with other metals in complex sulphides and as the chloride.

It is extracted from lead bullion by means of zinc, and purified by electrolysis or treatment with acid.

Silver has a specific gravity of 10.5. Atomic weight 108. Melting point 961°. It is the best conductor of heat and electricity.

Silver is **unaltered by pure air**, but is tarnished by sulphur compounds.

Silver is **alloyed** with copper for most uses. A double cyanide of potassium and silver is used for **electroplating**.

Silver nitrate is made by dissolving silver in nitric acid. It is the basis of other silver compounds.

The **silver halides** are insoluble compounds, and are made more easily reducible by the action of light. **Photographic plates** are coated with silver bromide, which, after exposure to the light, can be reduced by a developer. The unreduced silver bromide is dissolved by sodium thiosulphate.

Prints are made by exposing to light, under the negative, paper coated with silver bromide or chloride. Toning is the replacement of the deposited silver of the print by gold or platinum, by means of a chloride solution.

Gold occurs native, and alloyed with silver and other metals, and combined with tellurium.

It is separated by alloying it with mercury, or by dissolving it with cyanides.

Gold is the most **malleable** metal and is very **ductile.**

Gold has a specific gravity of 19.3. Atomic weight 197. Melting point 1062°.

It is unaltered by air or water, but dissolves in *aqua regia.*

Platinum occurs native, alloyed with similar metals.

It is unattacked by air, water, and acids, except *aqua regia.* Caustic alkalies, phosphorus, and some other elements attack it when hot.

Finely divided platinum is a powerful catalytic agent for certain purposes.

A colloid is a substance that forms uniform, permanent suspensions with liquids, and whose particles cannot pass through a dialyzing membrane.

EXERCISES

1. Why does not silver occur as an oxide?

2. Give the use of zinc, the cupel, and the electric current in the extraction of silver.

3. How much metallic silver can be obtained from 10 grams of silver nitrate by simple replacement?

4. Why is not silver commonly used as an electric conductor?

5. What is the compound formed when silver tarnishes?

6. What gas much used in the qualitative laboratory would discolor silver ornaments worn there?

7. What is horn silver? "Hypo"? Sterling silver? Lunar caustic? Oxidized silver?

8. In what respect does coin silver differ from pure silver? How does "Sterling" silver differ?

9. Compare the action of silver with concentrated sulphuric acid and that of zinc with dilute sulphuric acid.

10. Does coating glass with silver produce a better mirror than coating glass with tin amalgam? Discuss.

11. What use is made in the laboratory of the insolubility of silver chloride? Write an equation for its preparation.

12. How much silver nitrate can be made from a dime weighing 2.45 grams?

13. How could you prove the presence of copper in a silver coin?

14. Give the action of the developer, the fixing bath, and the toning solution in photography.

15. Why is it necessary to wash plates and prints for a long time after fixing?

16. Gold is less expensive than platinum. Why is it not used in the laboratory instead of platinum?

17. Give two characteristic properties and two important uses of (*a*) gold; (*b*) platinum.

18. Why do gold and platinum occur chiefly in an uncombined condition?

CHAPTER XXXIV

ALUMINUM AND ITS COMPOUNDS

449. Occurrence. — Aluminum never occurs in a free state, although it is one of the most abundant and widely distributed elements. Emery, corundum, ruby, and sapphire are more or less pure forms of aluminum oxide. Clay and the rocks by the decomposition of which it is formed consist chiefly of aluminum silicate. Two minerals of great importance in the preparation of metallic aluminum are bauxite, a hydrated oxide of aluminum, and cryolite, a fluoride of sodium and aluminum.

450. Preparation. — The only process used at present for the extraction of aluminum is an electrolytic one. The electrolyte consists of a solution of aluminum oxide in melted cryolite; the cryolite is not decomposed, but serves as a solvent only. The mineral bauxite is used to furnish the oxide. The cryolite is fused and kept liquid by the heat generated during the passage of the current; the dissolved aluminum oxide is separated into aluminum and oxygen by the current. The aluminum collects as a molten mass in the bottom of the melting pot; the oxygen is liberated at the anodes, which are oxidized by it. The weight of the anodes consumed about equals the weight of the aluminum liberated.

The apparatus consists of a rectangular iron box, lined with a thick layer of carbon which constitutes the cathode (Fig. 133). The outside dimensions are approximately

Charles Martin Hall (1863–1914) was the inventor of the electrolytic process by which aluminum is now produced. During his course in Oberlin College he became interested in aluminum and set about to find a cheap method of producing it. Failing in his attempts to use reducing agents, he turned to the electric current. His problem was to find a suitable solvent for aluminum oxide. He found that melted cryolite would serve this purpose, and after some preliminary difficulties, his process was established on a commercial basis. This process reduced the price of aluminum to about eighteen cents per pound. It is interesting to know that the same process was independently invented by Heroult in France. In March, 1911, Hall was awarded the Perkin Medal.

8 feet long, 4 feet wide, and 2 feet deep. Carbon rods about 3 inches in diameter and 18 inches long, placed in rows, serve as the anodes. These are so arranged that they can be lowered into the bath. The aluminum is allowed to run off at the base from time to time. The process is made continuous by the addition of fresh supplies of aluminum oxide as needed. The resistance of the

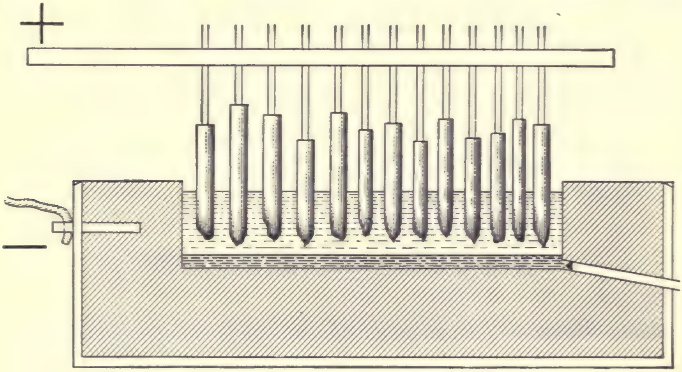


FIG. 133. — ELECTROLYTIC EXTRACTION OF ALUMINUM.

bath increases as the oxide is decomposed. The change in current operates a signal lamp which notifies the attendant that the bath needs aluminum oxide. Moist aluminum oxide is dried on a layer of fine coal that floats on the bath. The dry aluminum oxide is stirred into the bath from time to time, as it is needed.

451. Physical Properties. — Aluminum is a silver white metal, capable of a high polish. The dull surface usually seen is the result of a thin coating of the oxide. Aluminum is lighter than any other of the common metals, having about the same density as glass. It is malleable and ductile, but not very tenacious. It ranks next to silver, copper, and gold in thermal and electrical conductivity.

452. Chemical Properties. — Pure aluminum is practically unaltered in air. When aluminum powder or foil is strongly heated, it burns with a very brilliant light, resembling that of magnesium, and liberates a great deal of heat.

Aluminum is scarcely affected by nitric acid at any temperature. Dilute sulphuric acid acts very slowly with aluminum, with the liberation of hydrogen. With the concentrated acid it behaves somewhat like copper, liberating sulphur dioxide. It reacts readily with hydrochloric acid, forming aluminum chloride. Aluminum is also dissolved by sodium and potassium hydroxides, with the formation of the corresponding aluminates and the liberation of hydrogen:

$$2\,Al + 6\,KOH \longrightarrow 2\,K_3AlO_3 + 3\,H_2$$

453. Uses. — Aluminum has a wide range of uses, although the marked influence of a small amount of impurities has made its application more restricted than was thought probable at one time. Powdered aluminum is extensively used as a paint to protect other metals from corrosion and in flash powders for photography. Aluminum foil is replacing tin foil to a considerable extent. Many small useful and ornamental articles are made of aluminum. It is difficult to solder, so the parts of the larger articles are commonly welded together. Aluminum cooking utensils, when made of the pure metal, prove very satisfactory.

Aluminum is being used to a considerable extent in place of copper as an electric conductor. An aluminum wire, though larger than a copper wire of the same conducting power, is lighter and does not produce so great a strain on its supports. When the price of copper is high,

aluminum also makes the cheaper conductor of the two for carrying a given amount of current.

454. Aluminum Alloys. — Aluminum forms alloys with many of the metals. The most important is the alloy with copper, called *aluminum bronze.* This is hard, elastic, unaltered in air, easily cut, and has a color closely resembling gold. It has been successfully used in place of steel for small objects, such as watch springs and ball bearings. *Magnalium* is the trade name for an alloy of aluminum with magnesium and other metals. The metals used with aluminum and their proportions vary according to the use to be made of the alloy. It always contains 90% aluminum and less than 2% magnesium. The tensile strength of magnalium is much higher than that of aluminum, and it can be turned in a lathe. It is less corroded by air than aluminum, copper, zinc, or brass. On account of its superior strength this alloy is replacing aluminum for many purposes.

455. Thermit Process. — Aluminum is a very powerful reducing agent. Owing to this fact, we have a convenient means of obtaining metals such as chromium and manganese in the free state. When a mixture of aluminum powder and an oxide of the metal is ignited, a rapid combustion and a very high temperature result:

$$Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr$$

The *thermit process*, a very valuable method for repairing heavy iron machinery and for welding together the ends of rails or beams, is based on the same principle. Its value in this case is chiefly due to the high temperature (3000°) produced in the reduction of iron oxide by aluminum:

$$Fe_2O_3 + 2\,Al \longrightarrow 2\,Fe + Al_2O_3$$

This reduction takes place in a conical shaped vessel, from which the intensely hot iron flows into the crevice between the two pieces of iron to be joined.

456. Aluminum Oxide. — The occurrence of this compound, Al_2O_3, as corundum and emery, has already been mentioned. It is easily formed as a white, amorphous powder by igniting the hydroxide. Synthetic rubies, sapphires, and other gems can be artificially prepared by fusing aluminum oxide mixed with small quantities of compounds to give the desired color; potassium dichromate gives the ruby color, and a trace of titanium oxide produces the sapphire blue.

Emery, aluminum oxide mixed with various minerals, is extensively employed as an abrasive for grinding and polishing on account of its great hardness. An artificial corundum, made by fusing bauxite in an electric furnace, makes a better abrasive than the natural emery and is manufactured and sold under the name of alundum.

457. Double Salts. — If potassium sulphate and aluminum sulphate are mixed in water solution in the proportion of their molecular weights, a new substance having a very characteristic crystalline form and all the characteristics of a chemical compound is formed. This is the well-known substance *alum*, $KAl(SO_4)_2 \cdot 12\ H_2O$. It belongs to a class of substances known as *double salts*. Such salts contain two metals joined to one kind of acid radical.

458. Alums. — This class name is given to a series of double salts which have the same crystalline form as ordinary alum, similar chemical properties, and analogous formulas. They always contain a univalent metal and a trivalent metal. *Chrome alum* has the formula

$KCr(SO_4)_2 \cdot 12\ H_2O$; ammonium alum, $NH_4Al(SO_4)_2 \cdot 12\ H_2O$. The alums are much more soluble in hot than in cold water, and are deposited from a cooling solution in well-marked crystals, usually octahedral or cubical in form.

Ordinary alum is used for a *styptic* to check the flow of blood, and in the preparation of aluminum hydroxide for use in mordanting cloth and in clarifying water.

ALUMINUM HYDROXIDE

459. Preparation. — This is prepared by the addition of ammonium hydroxide to a solution of an aluminum compound. For example:

$$Al_2(SO_4)_3 + 6\ NH_4OH \longrightarrow 2\ Al(OH)_3 + 3\ (NH_4)_2SO_4$$

Calcium hydroxide may also be used. If sodium or potassium hydroxide is employed, it reacts in excess with aluminum hydroxide, forming an aluminate and water:

$$3\ KOH + Al(OH)_3 \longrightarrow K_3AlO_3 + 3\ H_2O$$

Aluminum hydroxide is an amorphous, translucent substance, insoluble in water. It reacts with acids, forming the corresponding aluminum salts; but, as we have just seen, it also reacts with strong bases in the manner of an acid. Aluminum hydroxide, $Al(OH)_3$ or H_3AlO_3, has, therefore, a double character, displaying one tendency or the other according to the nature of the substance with which it is reacting. This indicates ionization in two different ways:

$$Al(OH)_3 \rightleftarrows Al^{+++} + 3\ (OH)^-$$

$$H_3AlO_3 \rightleftarrows 3\ (H^+) + AlO_3^{---}$$

On heating, aluminum hydroxide is converted into aluminum oxide:

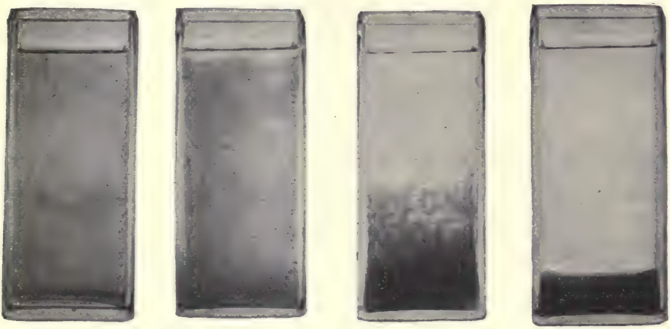
$$2\,Al(OH)_3 \longrightarrow Al_2O_3 + 3\,H_2O$$

460. Mordants and Lakes. — The amorphous character of the hydroxide renders it valuable in dyeing and water purification. Many dyestuffs do not readily enter the fiber of cotton goods, so it is necessary to use some substance to cause the dye to adhere and prevent it from washing off. Such a substance is called a *mordant.* It is found that when aluminum hydroxide is precipitated in a solution containing coloring matter, the color is carried down by the hydroxide as it settles, leaving the solution clear. The combination of the color and aluminum hydroxide is called a *lake;* lakes are used in dyeing and as pigments. In dyeing cotton, aluminum hydroxide is precipitated on the fiber, either by soaking the cloth first in alum and then in ammonium hydroxide solution, or by impregnating it with aluminum acetate, which yields the hydroxide on heating. The cloth, mordanted with aluminum hydroxide, is soaked in the dye, which forms an insoluble lake with the mordant, and thus produces a fast color. Other amorphous hydroxides, as those of iron and copper, are used as mordants.

Many mordants react chemically with the dye, producing new shades. So it is possible, by the use of the proper mordants, to secure different colors from the same dye. This is done in one method of calico printing, where the pattern is first stamped with a mordant. When the cloth is passed through the dye, the mordanted portions take it up and retain it, while the color is removed from the unmordanted parts by washing.

461. Coagulum in Water Purification. — The use of aluminum hydroxide in water purification is similar to that

in dyeing; it carries down with it suspended particles of foreign matter (Fig. 134). The hydroxide is produced



a *b* *c* *d*

FIG. 134. — COAGULUM IN WATER PURIFICATION.

a, water containing fine particles in suspension; *b*, aluminum hydroxide starting to form throughout water; *c*, aluminum hydroxide settling with the entangled suspended particles; *d*, purified water above settlings.

in this case by adding proper proportions of aluminum sulphate and lime:

$$3\,Ca(OH)_2 + Al_2(SO_4)_3 \longrightarrow 2\,Al(OH)_3 + 3\,CaSO_4$$

The aluminum hydroxide is completely removed by precipitation; the precipitate carries with it the greater part of the sediment and disease germs. The calcium sulphate is partly precipitated and partly dissolved, adding to the hardness of the water. In water containing a considerable amount of calcium, magnesium, or ferrous bicarbonates in solution, these salts are sufficient to precipitate the hydroxide; in such cases aluminum sulphate or alum is added to the water and the precipitation takes place without lime:

$$3\,CaH_2(CO_3)_2 + 2\,Al_2(SO_4)_3 + 6\,H_2O \longrightarrow 3\,CaSO_4 + 3\,H_2SO_4 + 4\,Al(OH)_3 + 6\,CO_2$$

$$3\,CaH_2(CO_3)_2 + 3\,H_2SO_4 \longrightarrow 3\,CaSO_4 + 6\,H_2O + 6\,CO_2$$

ALUMINUM SILICATES

462. Clay and Pottery. — Ordinary clay is an impure silicate of aluminum; *kaolin* is a pure form of a similar deposit. Both are formed by the decomposition of felspar rock. Felspar is a double silicate of aluminum and an alkali metal. When it is exposed to the action of the weather, the alkali silicate is removed by the water and carbon dioxide, and the residue left is *kaolin*, or clay containing other rock materials, as sand and mica. Pure kaolin is a white, pulverulent mass; when wet, it is plastic and can be molded. When the molded clay is heated and dried, it shrinks. Iron compounds often give clay a red color, seen in some bricks, and in roofing and drain tiles. Light brick is made from clay containing little or no iron. Clay containing silica is used for firebricks, stove linings, and crucibles.

Bricks, earthenware, porcelain, and china are made by molding the clay or kaolin into the desired form and baking in a furnace or *kiln* (Fig. 135). In making common earthenware articles, the baking temperature is not very high, and the mass being porous, as in flower pots, will not hold water. In making roofing tiles, jugs, and drain-pipes, salt is thrown into the fire; it volatilizes and forms on the surface of the articles a *glaze* impervious to water, consisting of a fusible silicate of sodium and aluminum.

Stoneware and crockery are made from purer varieties of clay, and are more carefully molded. In addition to the clay, they contain some fusible, hardening material.

FIG. 135. — KILN BEING FILLED WITH UNBAKED POTTERY.

A heavier and more durable glaze is used than that on earthenware.

463. Porcelain and china are made from pure kaolin, felspar, and quartz. The materials are ground fine,

thoroughly mixed, and wet. The wet mass is then modeled on a potter's wheel (Fig. 136) or molded in plaster of Paris molds and dried; when dry enough to handle, the mold is removed and the article smoothed. It is then *fired* at a low temperature which leaves it firm and hard, but porous and ready for the glaze. This consists of felspar and quartz ground fine and suspended in water. The article is dipped into the mixture and dried.

FIG. 136. — POTTER AT WORK.

It is then placed in a *seggar* or fire-clay box (Fig. 137, *b*) and supported on a tripod in such a way that it shall not touch the box. This is placed in the kiln, the temperature of which is gradually raised to a red heat, an operation requiring from twelve to twenty-four hours. The temperature is then increased for three days or more, and finally allowed to fall very slowly. The mass is now hard, dense, white, translucent, thin, and not easily affected by chemicals, except alkalies. The colors that are used in decorating china are composed of substances that are stable

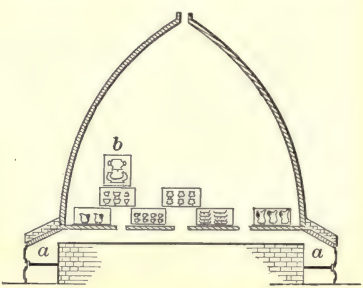


FIG. 137. — POTTERY KILN.
a, fire-box; *b*, seggars.

at the high temperature necessary for the fusion of the glaze.

464. Cement and Concrete. — Hydraulic cement results from the heating of a mixture of limestone (calcium carbonate) and clay (aluminum silicate) until they just begin to melt together. Many natural limestones contain the aluminum silicate mixed with the calcium carbonate in nearly the required proportions. Such cement rocks, when burned in a manner similar to that used in making quicklime (§ 357), yield *natural cements*. Artificial cements are made by "burning" clay or shale with marl, limestone, or chalk.

The rock materials are crushed in the proportion of about 1 part of silicate to 3 parts of carbonate, and finely powdered. After thorough drying, the mixture is burned in long, inclined, rotary kilns, through which it passes from the comparatively cool upper part to the intensely heated lower end. The lumps of the semi-fused material which issue are cooled and ground to an extremely fine powder. The quality of the cement depends to an important degree on the fineness of the grinding.

465. Setting of Cement. — Cement is believed to consist of a mixture of calcium silicate and calcium aluminate. When it is mixed with water and the mass allowed to stand, it solidifies or "sets." The reaction that takes place is probably a conversion of the calcium and aluminum silicates of the dry cement into other silicates of the same metals containing combined water. Calcium hydroxide is probably also set free during this reaction and hardens as it does in the parts of mortar that are not exposed to the air (§ 362). As the constituents of the air have no part in the setting of cement, it goes on as well

under water as in the air, and as fast in the inside of the mass as on the outside. The increase in hardness and strength goes on rather rapidly during the first few days after the cement is mixed with water, and then more slowly, but the cement continues to gain strength for years.

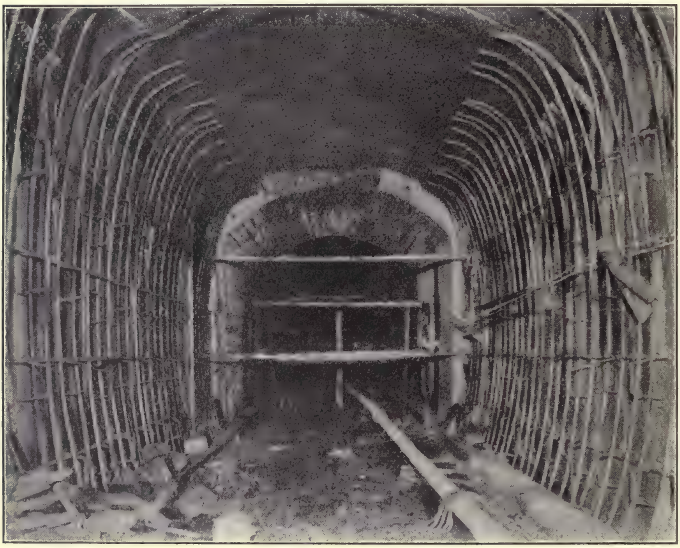


FIG. 138. — REËNFORCED CONCRETE CONSTRUCTION IN A NEW YORK SUBWAY.

466. Concrete; Reënforced Concrete. — The chief use of cement is in making concrete, a mixture of sand and broken stone or gravel with cement and water. Concrete is used for the foundations, floors, and walls of buildings, by pouring the wet concrete into forms made of board or steel. After it is thoroughly set, it gives a mass that has enormous strength in resisting pressure. This value may rise as high as 7000 pounds to the square inch. But concrete is not so resistant against *tensional* (pulling) stresses. To meet this need, twisted steel rods are set in

the molds in such way a that they become surrounded by and enveloped in the concrete (Fig. 138). Such structural work is known as *reënforced concrete.* Its use has revolutionized building processes in the last few years.

Concrete is indispensable for bridge piers and other work below water.

SUMMARY

Aluminum does not occur native. Its oxides and silicates are found widely distributed.

It is **prepared** by the electrolysis of oxide of aluminum dissolved in cryolite.

Aluminum is a silver-white metal; specific gravity, 2.6; melting-point, 657°. It is a good conductor of electricity.

Aluminum **dissolves** in hydrochloric acid and in potassium hydroxide.

It is **used** for making aluminum bronze, cables for conducting electricity, paint, flashlight powders, foil, ornamental articles, and cooking utensils.

Corundum, ruby, and sapphire are nearly pure **aluminum oxide** Emery is corundum mixed with iron.

Common (potash) **alum** has the formula $KAl(SO_4)_2 \cdot 12\,H_2O$. Other alums have the same crystalline form and analogous formulas. They always contain a univalent metal and a trivalent metal (or radical).

Aluminum hydroxide possesses the properties of a base and those of an acid.

It is used as a mordant and in the purification of water.

Clay is an impure silicate of aluminum and is used in the manufacture of bricks and of earthenware.

Kaolin, nearly pure aluminum silicate, is used in the manufacture of porcelain and of china.

Cement is made by heating to incipient fusion a mixture of limestone and clay. Cement hardens under water.

Concrete is a mixture of sand, broken stone, and gravel with cement and water.

Reënforced concrete is concrete in which steel rods are embedded to take up the tensional stresses.

EXERCISES

1. Would you carry on the electrolysis of sodium chloride in an aluminum dish? Would you concentrate a solution of nitric acid in an aluminum vessel? Would you concentrate a solution of potassium hydroxide in an aluminum cup? Explain.

2. Name three advantages in the use of aluminum for kitchen utensils.

3. For what purposes is aluminum bronze used?

4. Why is aluminum not used for the framework of bicycles and automobiles?

5. What would be the weight of a piece of aluminum containing a cubic foot? A cubic foot of water weighs 62.5 lb.

6. How much aluminum is contained in 200 tons of aluminum oxide?

7. Describe how the broken propeller shaft of an ocean steamer could be repaired by thermit. Show the economy of the process.

8. Write formulas for the following alums: sodium chromium alum, ammonium iron alum, potassium iron alum.

9. How much calcium hydroxide would be required to combine with 20 kilos of aluminum sulphate?

10. Compare the action of aluminum sulphate and copper sulphate in water purification.

11. Write an equation showing how aluminum hydroxide can play the part of a base; of an acid.

12. What compound of aluminum is formed when a solution of calcium bicarbonate reacts with a solution of aluminum sulphate?

13. What is a mordant? A lake?

14. What is meant by saying that aluminum hydroxide has an amorphous character?

15. What advantage has concrete in building foundations for bridge piers and dams?

16. Explain why steel rods are used in reënforced concrete.

17. Compare the hardening of cement with that of mortar.

18. How many liters of hydrogen would be liberated by the addition of 9 grams of aluminum to an excess of hydrochloric acid?

19. Describe or define briefly: alum, concrete, porcelain, emery, aluminum bronze.

CHAPTER XXXV

TIN AND LEAD

TIN was one of the earliest metals known. The Phœnicians obtained it from the British Isles, which they called Cassiterides, land of tin. As a constituent of bronze it was used before iron.

467. Metallurgy of Tin. — Tin oxide, SnO_2, is the only available ore. The present commercial supply comes principally from the Federated Malay States and Bolivia. Tin oxide is reduced by heating it in a reverberatory furnace with coal:

$$SnO_2 + C \longrightarrow Sn + CO_2$$

The molten metal which collects at the bottom of the furnace is drawn off and cast into ingots, known commercially as *block tin.* It is purified by heating it on the inclined hearth of a furnace. The less easily melted impurities remain, while the easily melted tin flows down the hearth. It is further purified by being poled, in the same way as blister copper.

468. Properties of Tin. — Tin is a white, lustrous metal, capable of withstanding the ordinary atmospheric agents. Being soft and malleable, it can be cut and hammered. Like zinc, it is crystalline in structure, and if a bar of tin is bent, it makes a peculiar noise (*tin cry*), probably caused by the friction of the crystals. Like zinc, its

physical properties vary considerably with the temperature. It melts at a rather low temperature, and burns, forming a white oxide.

With acids tin does not react like any *one* of the other metals ; with hot, concentrated hydrochloric acid, it forms *stannous chloride*, $SnCl_2$; with sulphuric acid it reacts like

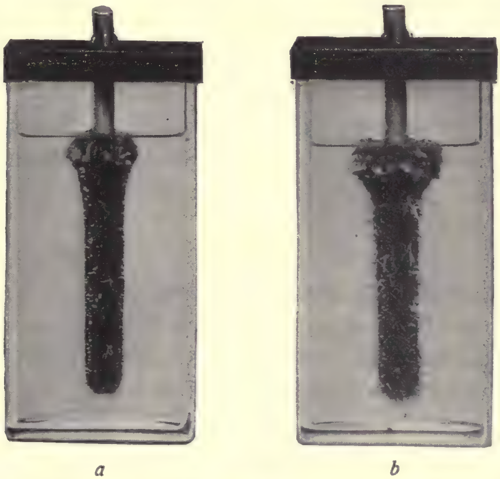


FIG. 139. — REPLACEMENT OF TIN BY ZINC.

a, five minutes after zinc has been placed in stannous chloride solution ; *b*, twenty minutes after.

copper ; nitric acid oxidizes it to a white, insoluble solid known as metastannic acid.

Tin can be separated from solutions of its compounds as a gray, spongy mass, by immersing a strip of zinc in the solution (Fig. 139) :

$$SnCl_2 + Zn \longrightarrow Sn + ZnCl_2$$

469. Uses of Tin. — The resistance of tin to ordinary corrosive agents is utilized in protecting other metals by

covering them with a layer of tin. Ordinary *tinware* is sheet iron, which has been thoroughly cleaned and dipped into melted tin. Copper vessels and brass pins are similarly treated.

Tin foil is tin, hammered or rolled into thin sheets; cheaper grades contain some lead. Pipes made of pure tin (*block tin*) are used to convey soda water and beer from the tanks to the faucet.

Many common alloys contain tin. Bronze contains copper, tin, and often zinc. The one cent piece is bronze. Pewter and solder contain tin and lead. Britannia metal and white metal contain varying proportions of tin, antimony, and copper. Anti-friction and fusible metals often contain considerable tin.

470. Compounds of Tin.—*Stannous chloride*, formed by the reaction of tin and hydrochloric acid, is the only common compound. The hydrated salt, $SnCl_2 \cdot 2\,H_2O$ is technically known as *tin crystals*, and is extensively used in mordanting. It produces more brilliant shades than the aluminum compounds. Stannous chloride is a strong reducing agent in acid or in alkaline solutions. Ferric salts are reduced by it to ferrous compounds:

$$2\,FeCl_3 + SnCl_2 \longrightarrow 2\,FeCl_2 + SnCl_4$$

Mercuric compounds are first reduced to mercurous salts, and with an excess of the reagent, to metallic mercury:

$$2\,HgCl_2 + SnCl_2 \longrightarrow 2\,HgCl + SnCl_4$$
$$2\,HgCl + SnCl_2 \longrightarrow SnCl_4 + 2\,Hg$$

The *stannic chloride*, $SnCl_4$, is a colorless, fuming liquid, which is readily decomposed by water.

Thus the valence of tin may be two or four, as shown

by the existence of stannous and stannic compounds. *Stannous sulphide*, SnS, is a brown, insoluble compound. *Stannic sulphide*, SnS_2, is a yellow, insoluble solid used as a pigment.

Cotton goods are rendered non-flammable and stronger by depositing metastannic acid on the fibers. The goods are dipped in a solution of sodium stannate (Na_2SnO_3), then into a solution of ammonium sulphate:

$$SnCl_4 + 6\,NaOH \longrightarrow Na_2SnO_3 + 4\,NaCl + 3\,H_2O$$
$$Na_2SnO_3 + (NH_4)_2SO_4 \longrightarrow H_2SnO_3 + Na_2SO_4 + 2\,NH_3$$

LEAD

Owing to the wide distribution of its compounds and the ease of separation from its ores, lead has been used by man from the earliest times.

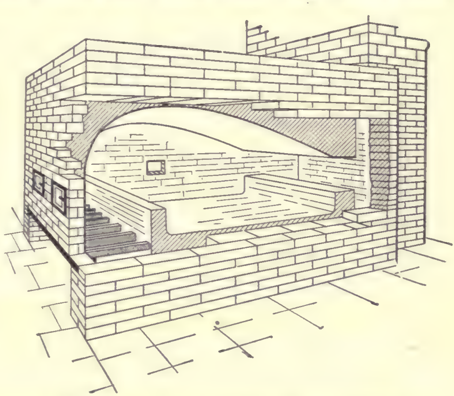


FIG. 140. — REVERBERATORY FURNACE.

471. Metallurgy. — The most common ore is the sulphide, galena, PbS, large deposits of which are found in Missouri, Illinois, and Colorado. The method employed in the extraction depends largely upon the purity of the ore.

Ores having a large percentage of lead are roasted in a reverberatory furnace (Fig. 140) until two thirds of the sulphide has been oxidized, forming lead oxide, sulphur dioxide, and some lead sulphate:

$$2\,PbS + 3\,O_2 \longrightarrow 2\,PbO + 2\,SO_2$$
$$PbS + 2\,O_2 \longrightarrow PbSO_4$$

When the oxidation has proceeded far enough, the air is shut off by closing the doors, and the mixture is heated to a higher temperature. The remaining lead sulphide now reacts with the lead oxide and sulphate, forming lead and sulphur dioxide:

$$PbS + 2\,PbO \longrightarrow 3\,Pb + SO_2$$
$$PbS + PbSO_4 \longrightarrow 2\,Pb + 2\,SO_2$$

The lead is molded into ingots known as *pig lead.* When there is a considerable amount of precious metal in the lead, it is known as *base bullion.* The working of this has been described under silver (§ 426, Parkes' process).

Ores poor in lead are reduced in a blast-furnace similar to that used for copper; indeed, they may be separated from the ore at the same operation, the heavy lead settling beneath the matte and slag.

Electrolytic reduction of galena is effected in a bath of dilute sulphuric acid. The crushed galena is made the cathode, the bottom of the pan the anode. The lead is obtained as a spongy mass. The hydrogen sulphide produced is conducted away to a combustion chamber and converted into sulphuric acid or sulphur.

472. Properties of Lead. — Lead is a soft, bluish white metal. The brilliant luster, apparent when freshly cut, soon disappears, owing to the formation of a thin film of oxide. This coating, however, protects it from further change. Lead is not very tenacious, but being soft it can be rolled into sheets or forced through a die to form pipe.

When heated in air, lead oxidizes. Neither cold hydrochloric nor sulphuric acid has much effect on it. Nitric

acid, acetic acid (from vinegar), and many vegetable acids dissolve it, forming soluble salts. Water containing carbon dioxide corrodes lead, hence the objection to lead waterpipes, since the water by this action might carry away poisonous lead compounds in solution.

All lead compounds are poisonous, and if taken into the system cause serious illness. Even minute quantities in the water will ultimately produce this result, for lead compounds are excreted with difficulty, and therefore accumulate in the body. Painter's colic is a form of chronic lead poisoning.

On immersing a strip of zinc in a solution of a lead salt, the lead separates in a characteristic crystalline deposit, the *lead-tree* (Fig. 141):

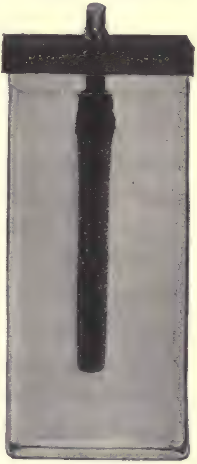


FIG. 141. — REPLACEMENT OF LEAD BY ZINC.

$$Pb(NO_3)_2 + Zn \longrightarrow Zn(NO_3)_2 + Pb$$

The formation of insoluble chrome yellow by addition of potassium chromate to a solution of a lead salt is another characteristic property of lead salts:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2\,KNO_3$$

473. Uses of Lead. — Lead is very extensively used for pipes and as a sheathing for cables, as it is easily cut, bent, or soldered. Lead pipe is now made by forcing the hot lead through a die by a piston. The opening of the die is partly obstructed by a solid cylindrical rod attached to the upper surface of the piston. This rod moves upward with the piston, and the pipe is formed by the lead being squeezed out between the rod and the wall of the die.

Sheet lead was formerly used for roof covering much more than at present. It is very widely used as a lining for tanks, cisterns, and cells used in electrolytic operations. The Chinese have long used it for lining tea chests.

Thin sheet lead, alloyed with tin, is often used instead of pure tin foil. *Type metal* contains lead, with tin and antimony which harden it and form an alloy that expands in solidifying. Thus it fills the molds and makes a clear-cut type. *Solder* and fusible metals are largely lead and tin. Such alloys are forced through a die in the same manner as lead pipe, forming a wire used as *fuse wire*.

Large quantities of lead are used in the manufacture of *shot*. As already stated, the shot contains a small amount of arsenic. The molten metal is run into a perforated vessel, and falls in streams from a considerable height into the water. In falling, the streams separate into drops, which solidify before they reach the water. The sizes of shot are assorted by allowing them to run down inclined planes and over screens of different meshes. The smallest shot fall through the nearest (smallest) openings into the bins, the larger shot going on to the larger holes. Irregular shaped pieces will not roll well, and are finally pushed off at the end. The shot are polished by tumbling them in a barrel or drum with a little graphite.

COMPOUNDS OF LEAD

474. Oxides.—*Lead oxide*, PbO, when of a yellowish tint, is known as massicot; when it solidifies from the molten state it is buff-colored and crystalline, and is known as *litharge*. The presence of bismuth sometimes gives the litharge a yellowish color. Litharge is made by heating lead in the air. Considerable quantities are produced in

the cupellation of silver. It is largely used in the preparation of oils and varnishes, of glass and glazes, and of other compounds of lead. A mixture of litharge and glycerine is used as a cement, especially for stone and glass.

Red lead, or minium, is a bright red powder, known as American vermilion. It is prepared by heating lead or lead oxide in the air, oxygen being absorbed in the operation. The tint and composition often vary with the manipulation. Its composition may be represented by the formula: Pb_3O_4 or $(2\,PbO \cdot PbO_2)$. It is used in making flint glass and as a pigment, especially on ironwork. Being an oxidizing agent, it hastens the hardening of the oils used in paint. On this account a mixture of red lead and oil is used by plumbers and gas fitters to make tight joints.

Lead dioxide, PbO_2, also called lead peroxide, is a brown powder obtained by treating red lead with nitric acid. It is used as an oxidizing agent on the positive plates of storage batteries.

475. White Lead, or *basic lead carbonate*, is a heavy, white, opaque powder. It mixes well with linseed oil and forms a valuable paint base. The body of many paints is white lead, which furnishes opacity or *body*, different colors being produced by the addition of colored pigments. Owing to the importance of white lead, many methods have been devised for its production.

The *Dutch process of corrosion* has been in use three hundred years, and although details have been improved, remains essentially the same. Ridged and perforated disks, or "buckles," of lead (Fig. 142) are piled in a loosely covered earthenware pot, the lower part of which contains a little dilute acetic acid. Such pots are placed side by side and covered with moist tan bark; other layers

of pots are added to a considerable height. The decaying organic matter generates heat and carbon dioxide. The acetic acid is volatilized, forming basic lead acetate. The carbon dioxide resulting from the fermentation changes this to the basic carbonate. Three or four months are required for the complete corrosion of the lead; the right-hand portion of Fig. 142 represents a jar broken open to show the lead buckles after corrosion. The white lead is removed from the jars, and small pieces of unaltered lead are removed by screening. It is then ground wet, washed, strained through fine silk sieves, and allowed to settle. The white lead is finally ground in oil and is ready for use. The corrosion process requires much time but yields good paint. The Dutch process aims at a white lead with the composition $Pb(OH)_2 \cdot 2\,PbCO_3$, but the composition of the product varies.

FIG. 142.

A much quicker corrosion is obtained by blowing the melted lead into a fine spray by a blast of steam, and treating the resulting powder with a stream of carbon dioxide in the presence of moist air and acid, in a rotating cylinder.

The commercial white paints are generally mixtures of white lead and zinc white. Calcium carbonate, barium sulphate, silica, and other substances are frequently used as extenders.

476. Chrome Yellow. — *Lead chromate*, $PbCrO_4$, is an insoluble, bright yellow powder, prepared by mixing solutions of lead salts and chromates. It is used in dyeing and painting.

SUMMARY

The chief ore of **tin** is the oxide, which is reduced by heating with coal.

Tin is soft, malleable, and crystalline. Its specific gravity is 7.3, and it melts at 232° C.

It is **unaltered by air** at ordinary temperatures.

Tin is **used** for pipe, as foil, and as a coating for iron. It is a constituent of bronze, pewter, and white metal.

Stannous chloride is formed by the action of hydrochloric acid on tin. It is a reducing agent.

Lead occurs chiefly as a sulphide. The ore is reduced in a reverberatory furnace, or by electrolysis.

Lead is soft, malleable, and tenacious. Its specific gravity is about 11.3 and its melting point 327° C.

It oxidizes in air and dissolves in nitric and acetic acids. Water containing carbon dioxide corrodes it, producing poisonous compounds.

Lead is **used** for pipe, as a lining, a covering material, and in alloys, such as type metal, solder, and shot.

Lead oxides are made by heating lead in air. They are used in making varnishes and glass, and as pigments. Lead dioxide is used in storage batteries.

White lead is basic lead carbonate. Chrome yellow is lead chromate.

EXERCISES

1. Which forms the better protective coating for iron, — tin or zinc?

2. State the relative advantages of lead and tin plate as a coating for roofs.

3. Why were lead and tin early obtained in the metallic state?

4. Why is tin foil superior to lead foil for wrapping articles of food?

5. Why is arsenic put in shot?

6. What is litharge? Red lead? White lead?

7. Why is red lead called a drier in paints and varnishes?

8. What advantage has zinc white over white lead as a paint base? White lead over zinc white?

9. What are the characteristic properties of glass containing lead?

10. How much lead can be extracted from a ton of galena?

11. In converting a ton of lead oxide (PbO) into red lead (Pb_3O_4), how much oxygen is absorbed?

CHAPTER XXXVI

MANGANESE, CHROMIUM, COBALT, AND NICKEL

MANGANESE

477. Preparation and Properties. — The most important ore of manganese is pyrolusite, which is crude manganese dioxide. The metal is obtained by igniting a mixture of pyrolusite and aluminum powder. Heat is applied at one point and the action spreads through the whole mass:

$$3\,MnO_2 + 4\,Al \longrightarrow 2\,Al_2O_3 + 3\,Mn$$

Manganese is a hard metal resembling steel in appearance. It oxidizes in moist air and, when finely divided, decomposes boiling water. It dissolves readily in sulphuric and hydrochloric acids, with the liberation of hydrogen and the formation of the corresponding salt of the manganous ion, Mn^{++}:

$$Mn + H_2SO_4 \longrightarrow MnSO_4 + H_2$$

Its alloys with iron, ferro-manganese, and spiegeleisen are used in the production of Bessemer iron and steel.

478. Manganese Compounds. — Manganese forms several oxides, of which the most important is the *dioxide*, MnO_2. This is a hard, black solid which conducts electricity. It is a powerful oxidizing agent, as we have already seen in the preparation of chlorine from hydrochloric acid (§ 75). Its conducting power and oxidizing action make it a valuable depolarizer in voltaic cells.

The manganous salts are stable compounds, whose water solutions are pink. The salts of the manganic ion Mn^{++++} are unstable.

479. Manganates and Permanganates. — Since manganese is one of the elements that display both metallic and non-metallic characteristics, we have salts in which it occurs as a constituent of the negative ion.

The most important of these salts are the manganates and the permanganates, both of which contain the radical MnO_4. In the manganates the ion is bivalent, MnO_4^{--}; in the permanganates it carries only one charge, MnO_4^{-}. Corresponding to this difference in valence of the ion are differences in the properties of the salts. The manganates are green and the permanganates are purple.

Potassium manganate is made by fusing a manganese compound with potassium hydroxide in the presence of air or an oxidizing agent, dissolving the residue and evaporating the solution in a vacuum. The crystals obtained are dark green. They are decomposed by water, with the liberation of manganese dioxide and the formation of potassium permanganate, $KMnO_4$:

$$3\,K_2MnO_4 + 2\,H_2O \longrightarrow 2\,KMnO_4 + MnO_2 + 4\,KOH$$

Potassium permanganate is obtained as dark purple crystals, which dissolve in water, yielding a violet solution. It is a powerful oxidizing agent.

CHROMIUM

480. Chromium occurs chiefly as chromite, $Cr_2O_3 \cdot FeO$. From this it is reduced by aluminum in a manner analogous to that employed in the preparation of manganese. It is a hard, steel-gray metal, unaltered by the air.

When very small quantities are added to steel, the tenacity and hardness are increased.

481. Oxides of Chromium. — The two important oxides of chromium are *chromic oxide*, Cr_2O_3, and *chromic anhydride*, CrO_3. The chromic salts are derived from chromic oxide; the most important is the double sulphate of potassium and chromium, $KCr(SO_4)_2 \cdot 12\,H_2O$, known as *chrome alum*. A solution of chromic anhydride yields CrO_4^{--} ions, but the acid is isolated with difficulty, as it breaks up into chromic anhydride and water. The solution of the anhydride is a powerful oxidizing agent, and its derivatives, the chromates and dichromates, resemble it in this respect.

482. Chromates and Dichromates. — *Potassium dichromate*, $K_2Cr_2O_7$, is the source of most of the chromium salts. It is prepared by heating chromite with potassium carbonate and lime in a reverberatory furnace. It forms large red crystals from solution or fusion; these are somewhat soluble in cold water, and their solubility increases rapidly as the temperature rises. Potassium dichromate reacts with sulphuric acid in the presence of an oxidizable substance, with the formation of chromium sulphate and the liberation of oxygen. This oxidizing action is frequently made use of in depolarizing voltaic cells. Sodium dichromate is very similar to potassium dichromate, but has the added advantage of being more soluble. Most of the dichromates are orange in solution.

Potassium chromate, K_2CrO_4, is prepared by the addition of potassium hydroxide to the dichromate:

$$K_2Cr_2O_7 + 2\,KOH \longrightarrow 2\,K_2CrO_4 + H_2O$$

It forms yellow crystals, more soluble than those of the dichromate.

The acids from which the chromate and the dichromate are theoretically derived have the formulas H_2CrO_4 and $H_2Cr_2O_7$ respectively. *Both* of these have the anhydride CrO_3, as may be seen from the theoretical equations:

$$H_2O + CrO_3 \longrightarrow H_2CrO_4$$
$$H_2O + 2\,CrO_3 \longrightarrow H_2Cr_2O_7$$

The relation between the chromate and the dichromate is shown if the formula of potassium dichromate is written $K_2CrO_4 \cdot CrO_3$. Other complex chromates are known containing more than one CrO_3 group.

Lead chromate, $PbCrO_4$, made by treating a soluble lead salt with a chromate or dichromate, is a yellow, insoluble compound, known as chrome yellow, and used as a pigment. The chromates of zinc and barium are also used as pigments.

483. Change of Valence through Oxidation. -- In cases of elements which have, like manganese and chromium, a wide variety of compounds, the change of the element from one compound into another is frequently accompanied by a change of valence. We will consider the case of chromium briefly.

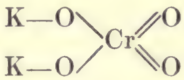
Chrom**ous** chloride, $CrCl_2$, in which the valence of the metal is 2, can be changed into chrom**ic** chloride, $CrCl_3$, where the valence is 3, by an oxidizing agent. The presence of hydrochloric acid enables us to write a simpler equation:

$$2\,CrCl_2 + 2\,HCl + O \longrightarrow 2\,CrCl_3 + H_2O$$

Chromic compounds can be converted into chromates by melting them with a base and an oxidizing agent, such as potassium chlorate:

$$2\,CrCl_3 + 10\,KOH + 3\,O \longrightarrow 2\,K_2CrO_4 + 6\,KCl + 5\,H_2O$$

The valence of chromium in potassium chromate is shown to be 6 by the following diagram of the arrangement of the atoms:



Hence it appears that in the reaction given, chromium has again undergone a change in valence brought about by an oxidizing agent.

Reducing agents produce reverse changes.

These facts represent a general principle which may be stated thus: *Oxidizing agents tend to produce actions in which valence is raised; reducing agents tend to produce actions in which valence is lowered.*

The change of chromates into dichromates, and the reverse changes, do not involve changes of valence, since both salts are derived from the same anhydride.

NICKEL

484. Occurrence. — The greater part of the nickel that the world uses comes from the province of Ontario in Canada, and from New Caledonia. The nickel compounds in the ores form only a small part of the whole. The Canadian ore is chiefly a sulphide of iron, containing about 2% each of nickel and copper. Nickel is nearly always a constituent of meteoric iron.

485. Extraction. — The sources of nickel are complex minerals, chiefly sulphides and arsenides mixed with large quantities of other materials. The separation of nickel from such mixtures presents a complex problem. The low percentage of nickel contained in the ore makes it necessary to produce, by methods of concentration, a sub-

stance containing a higher percentage of nickel before processes for smelting are carried on. To accomplish this, use is frequently made of the fact that nickel has a greater affinity for arsenic than any of the metals with which it is found associated, and of the fact that nickel stands next to copper in its affinity for sulphur.

If the ore contains no copper, or in case the copper is to remain alloyed with the nickel, it is usual to make either (*a*) nickel matte, or (*b*) nickel *speiss*.

Nickel matte is made when the ore consists of sulphides. The process is similar to that described (§ 415) for the production of copper matte. Nickel matte contains about 40 % of nickel, and is a mixture of sulphides.

Nickel speiss is made when the ore is a mixture of arsenides; it is itself a complex arsenide of nickel, iron, and frequently of other metals. The process of making it resembles that used for the production of matte, and it contains from 40 % to 50 % nickel. In case copper is to be eliminated, one of the simpler methods takes advantage of the affinity of copper for sulphur and of nickel for arsenic. The compounds formed are but slightly soluble in each other.

The nickel matte (or the nickel speiss) is then converted into nickel oxide by oxidation in a reverberatory furnace or a converter. The production of arsenic oxide, a substance which is highly poisonous and which is injurious to vegetation, is avoided by using a mixture of sodium carbonate and sodium nitrate to convert the arsenic into sodium arsenate, which is readily removed by dissolving in water.

The nickel oxide is reduced by mixing it with flour paste, rolling and cutting the mixture into small cubes, which are dried, embedded in charcoal, and heated. The nickel cubes thus obtained are suitable for making alloys, but are too impure for nickel ware.

The Mond method is used for the production of pure nickel from the ore. This method is based on the fact that nickel will combine directly with carbon monoxide to form nickel carbonyl, $Ni(CO)_4$. Nickel oxide, produced in smelting the ore, is reduced to nickel in a porous form by heating in the presence of hydrogen. Carbon monoxide at a temperature of 100° C. and a pressure of 15 atmospheres is then passed over the porous nickel to convert it into nickel carbonyl. The vapors of nickel carbonyl are decomposed by heating them to 200° C. under atmospheric pressure. The carbon monoxide is recovered for the conversion of a new lot of nickel into nickel carbonyl. The direction in which the reversible equation

$$Ni + 4\,CO \rightleftarrows Ni(CO)_4$$

runs depends upon temperature and pressure.

486. Properties of Nickel.—Nickel is a hard metal, malleable, possessing a high melting point, and resembling silver in color. It is capable of receiving and retaining a very high polish. Dry air does not attack it. Like cobalt, it dissolves readily in nitric acid, but is only slowly attacked by hydrochloric and sulphuric acids. Nickel-plated ware should never be scoured, but should be cleaned by washing with soap suds and burnishing with a cloth.

Solutions of nickel salts have a beautiful, characteristic green color. Nickel and cobalt resemble iron in being attracted by a magnet. Their chemical properties are also similar to those of iron.

487. Uses.—Nickel is of considerable practical importance because of its silver-white color and the fact that it does not readily tarnish in air. It is chiefly used as a covering for other metals. It is deposited by an electrolytic

process similar to that used in silver or copper plating. Nickel is a constituent of several important alloys. *Nickel steel*, which contains about 5% nickel, is both hard and tough; it is used in making armor plates for battle ships. *Nickel coins* contain about one part nickel to three parts copper.

488. Compounds. — The sulphate, $NiSO_4$, and a double sulphate of nickel and ammonium are the salts used as electrolytes in nickel plating.

COBALT

As no industrial use is made of pure cobalt, the metal is seldom extracted.

489. Cobalt Ores. — Cobalt is found as a minor constituent of ores of complex composition. These ores are usually sulphides or arsenides, in which iron is the predominating metal, though they contain copper and nickel as well. Cobalt speiss, $CoAs_2$, is found in Saxony; cobalt glance, $CoAs_2 \cdot CoS_2$, in Norway and Sweden. The ores are usually worked up to obtain cobalt compounds without separating the element in the metallic state. They are first roasted to remove sulphur and arsenic, and the resulting oxides are then dissolved in acids.

490. Properties of Cobalt. — Cobalt is a hard, magnetic metal, malleable and ductile, and capable of receiving a high polish. Its melting point, like that of iron, is high. It dissolves readily in nitric acid, but is acted on slowly by other acids. Solutions of cobalt salts have a rose color.

491. Cobalt Compounds. — The chloride, $CoCl_2$, and the nitrate, $Co(NO_3)_2$, are of some importance. The chloride has a peculiar property of changing its color when ex-

posed to air of varying humidity. These changes are explained by the fact that the substance forms a number of different compounds with varying amounts of water of crystallization and passing readily into one another. The less hydrated forms are blue or lavender, while the more hydrated are red. Heated or exposed to dry air, the red salt loses water of crystallization, and is changed to a blue, less hydrated form. Advantage is taken of this fact to make "sympathetic ink," which is invisible until heated, and for simple apparatus to indicate the amount of moisture in the air.

Cobalt nitrate, $Co(NO_3)_2$, is sometimes used in analytical work in testing for certain metals. It unites with certain metallic oxides, forming characteristically colored compounds. Thus aluminum compounds, when converted into the oxide by heating with the blowpipe, give a blue coloration when further heated with cobalt nitrate solution.

Cobalt sulphide, CoS, black in color, is precipitated from alkaline solutions of cobalt salts by hydrogen sulphide. Like iron, cobalt forms two double cyanides with potassium, $K_4Co(CN)_6$ and $K_3Co(CN)_6$.

SUMMARY

Manganese

Manganese occurs chiefly as pyrolusite, crude manganese dioxide.

Manganese alloys, ferro-manganese and spiegeleisen, are much used in the steel industry. Several forms of iron and steel contain manganese.

Manganese dioxide, MnO_2, insoluble, and potassium permanganate, soluble, are two important **oxidizing agents**.

Chromium

Chromium occurs less abundantly than manganese, chiefly as chromite, $Cr_2O_3 \cdot FeO$.

Chromium is used in making **chrome steel,** a very hard and tenacious alloy.

Important **chromium compounds** are: chromic oxide, Cr_2O_3, used as a green pigment; chrome alum, $KCr(SO_4)_2 \cdot 12\,H_2O$, used in tanning; lead chromate, $PbCrO_4$, used as a yellow pigment; potassium chromate, K_2CrO_4, and potassium dichromate, $K_2Cr_2O_7$, used as oxidizing agents.

A **wide variety of compounds** are formed by both manganese and chromium. This is due to two facts: (*a*) both elements display both metallic and non-metallic characteristics; (*b*) both elements display several different valences.

In causing elements to change through a series of compounds oxidizing and reducing agents play an important part. **Oxidizing agents tend to raise valence, reducing agents to lower it.**

Nickel

When a **nickel ore** contains arsenic, nickel will take arsenic from the other metals until it is satisfied. During the process a portion of the other metals will be oxidized and the oxides will pass into slag. When copper is not present a similar statement is true concerning the behavior of nickel towards sulphur.

A substance rich in nickel arsenide is known as **nickel speiss.**

Nickel matte is a substance rich in nickel sulphide.

Nickel oxide is obtained from nickel speiss or from nickel matte by oxidation in a furnace.

Cubes of somewhat impure nickel are formed by reducing nickel oxide by mixing it with flour and heating in charcoal.

Pure nickel is obtained by making use of the facts that carbon monoxide under pressure and at a temperature of 100° C. con-

verts nickel into nickel carbonyl ($Ni(CO)_4$) and that the vapor of nickel carbonyl decomposes at 200° C.

Nickel **does not tarnish in dry air** and is **used** for making alloys and as a protective coating for iron.

Cobalt

Metallic cobalt is rarely extracted.

Important **cobalt compounds** are the chloride, nitrate, and sulphide.

EXERCISES

1. How is manganese obtained in the free state from pyrolusite?

2. Why is spiegeleisen used in making Bessemer steel?

3. Why is manganese dioxide mixed with carbon in a dry cell?

4. Which is the easier to preserve, potassium manganate or potassium permanganate? Why?

5. What qualities does chromium give to steel? For what purposes is chrome steel suited?

6. Explain the relation between potassium chromate and potassium dichromate.

7. Why is the change of chromous into chromic chloride spoken of as oxidation?

8. During the smelting of nickel ores, what is the object in producing nickel speiss or nickel matte?

9. How is nickel speiss converted into nickel oxide?

10. How would nickel oxide be treated if the nickel were to be used for making alloys? For making nickel ware?

11. Why is iron often plated with nickel?

12. Name an acid in which nickel dissolves readily.

13. Name three metals that are attracted by a magnet.

14. Explain the action of sympathetic ink.

CHAPTER XXXVII

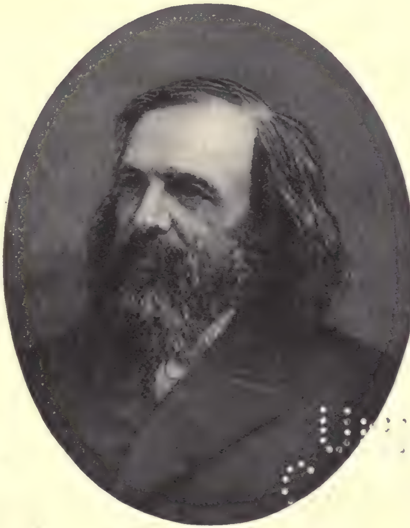
THE PERIODIC LAW

492. Early Attempts at Classification. — The discovery of new elements and the investigation of their properties led the earlier chemists to recognize the existence of certain families or groups of elements. In 1829 Döbereiner called attention to certain *triads* or groups of three elements in which the atomic weight of the second element was the arithmetical mean of the first and third. He also pointed out that the properties of the middle element were intermediate between those of the other two. This was the first attempt to show that a relation existed between the properties of elements and their atomic weights. The elements chlorine, bromine, and iodine form a well-marked triad:

$$\frac{35.5 + 127}{2} = 81.2;$$

the atomic weight of bromine, 80, approximates the mean, 81.2.

Other attempts to classify the elements were made from time to time, but it was not until 1860–1870 that any system received recognition. In 1863–1864 Newlands, an Englishman, directed attention to the fact that the elements showed surprising regularity when arranged in order of their atomic weight. He said the properties of each element seemed to be repeated in a measure by those of the eighth element following it. This relation is called



Dimitri Ivanovitch Mendelejeff (1834–1907) was born in Tobolsk, Siberia. Through the efforts of his mother, who established a glass works, he received an excellent education in Tobolsk and St. Petersburg. He spent the greater portion of his life as Professor of Chemistry in the University of St. Petersburg, and to him Russia owes the training of two generations of chemists, as well as the development of its petroleum and other chemical industries. Although there was no section of the chemical science of his time which was not enriched by his contributions, the fame of Mendelejeff rests secure on the setting forth and establishment of the Periodic Law.

the *law of octaves*. Newlands' system of classification, although it contained many of the principles we use to-day, attracted little notice. Lacking a strong advocate to push its claim, the new system was soon forgotten. In 1869 Mendelejeff, a Russian chemist, aroused great interest in scientific circles by bringing forward a system of classification which for the first time brought all the elements into a comprehensive scheme of relationship based upon their atomic weights. A few months later, Lothar Meyer, a German, put forward a similar system which he had worked out independently of Mendelejeff. Although Meyer has done much to assist in classifying the elements, it is now generally acknowledged that Mendelejeff is entitled to the greater credit, and the system we use to-day bears the name of the Russian chemist. It was Mendelejeff who brought forward a system which he elaborated and successfully defended against the many attacks made upon it.

493. Periodic Law. — Beginning with lithium, let us arrange the elements in the order of their atomic weights:

Lithium	Glucinum	Boron	Carbon	Nitrogen	Oxygen	Fluorine
7	9	11	12	14	16	19

Lithium is an element with strong metallic or basic properties; glucinum, Gl, is less metallic; boron has some metallic properties, but generally acts like a non-metal; carbon forms weak acids; nitrogen shows stronger acid properties; oxygen is characteristically acid; fluorine, at the end, is the most pronounced acid element. Hence, the seven elements show a gradation in properties from a pronounced metal to an element of strongly acid character. A similar transition can be shown for other properties as we pass from lithium to fluorine. Thus the

PERIODIC CLASSIFICATION OF THE ELEMENTS

	Series 0	Series I	Series II	Series III	Series IV	Series V	Series VI	Series VII	Series VIII
	R	R_2O ROH	RO $R(OH)_2$	R_2O_3 $R(OH)_3$	RO_2 $R(OH)_4$	R_2O_5 RO_4H_3	RO_3 RO_4H_2	R_2O_7 RO_4H	RO_4 ← Oxide ← Hydroxide
1	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	
2	Ne 20	Na 23	Mg 24.3	Al 27	Si 28.3	P 31	S 32	Cl 35.5	
3	A 39.9	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe Co Ni 56 58.9 58.7 Cu 63.6
4	—	(Cu 63.6)	Zn 65.4	Ga 70	Ge 72.5	As 75	Se 79.2	Br 80	
5	Kr 82.9	Rb 85.4	Sr 87.6	Y 89	Zr 90.6	Cb 93.5	Mo 96	—	Ru Rh Pd 101.7 103 106.7 Ag 108
6	—	(Ag 108)	Cd 112.4	In 115	Sn 119	Sb 120	Te 127.5	I 127	
7	X 130	Cs 133	Ba 137.4	La 139	Ce 140.2	—		Sa 150.4	
8	—	—	—	—	Er 167.7	—	—	—	
9		—	—	Yb 172	—	Ta 181.5	W 184	—	Os Ir Pt 191 193 195 Au 197
10		(Au 197)	Hg 200	Tl 204	Pb 207	Bi 208	—	—	
11	Nt 222.4	—	Ra 226	—	Th 232	—	U 238.5	—	

properties seem to vary with the atomic weights, or, in mathematical language, the properties are functions of the atomic weights. Sodium, the eighth element after lithium, closely resembles it, and may be placed directly beneath as the beginning of another horizontal row:

Lithium 7	Glucinum 9	Boron 11	Carbon 12	Nitrogen 14	Oxygen 16	Fluorine 19
Sodium 23	Magnesium 24	Aluminum 27	Silicon 28	Phosphorus 31	Sulphur 32	Chlorine 35.5

Magnesium resembles glucinum in its properties, and the characteristics of boron recur modified in aluminum. That is, the eighth element repeats the properties of the one taken as the first. Silicon, then, should be like carbon, and phosphorus should resemble nitrogen. These we know to be facts. Since the properties recur or are repeated at regular intervals, the properties are said to be periodic; or, as Mendelejeff expressed it, "a periodic repetition of properties is obtained if all the elements be arranged in the order of the atomic weights."

494. Long and Short Periods. — The table on the opposite page is arranged according to the principle of classification just given. Omitting for the present the first vertical column marked Series 0, the seven elements, from lithium to fluorine, form a horizontal series known as a *short period*. The set of elements from sodium to chlorine make the second short period. Beginning in the next line with potassium, it is found that the metallic properties do not disappear so rapidly as in the first and second short periods. Manganese, the seventh element, has some well-marked metallic properties. Iron is not placed under potassium, but is put in an eighth series together with cobalt

and nickel. There is a gradual increase in the metallic properties as we pass through these three elements to the more metallic copper. The elements from copper to bromine show a gradual decline in the metallic properties and an increase in the acid properties until the strongly acid element bromine is reached. Hence we have a series of seventeen elements, beginning with potassium and ending with bromine. This is known as a *long period*. The elements from rubidium to iodine constitute the second long period. In this period the elements of the eighth series, ruthenium, rhodium, and palladium, form a bridge in the transition of properties from the seventh series to the first.

495. Families or Groups of Elements.—It is evident from the periodic nature of the classification that all the elements in one of the vertical series have certain resemblances. The relationship, however, is much closer in some cases than in others. Thus, in Series II, calcium, strontium, and barium are more closely allied to each other than they are to magnesium, zinc, cadmium, and mercury. These last four elements form a closely related group. That is, the more closely related elements are not successive, but alternate in a vertical series. The result of this alternate arrangement is to divide each vertical series into two families or groups. In Series VI, chromium and molybdenum are in one family, while sulphur, selenium, and tellurium form the other. The halogen elements, chlorine, bromine, and iodine, in Series VII, afford one of the best examples of a closely related group. Lithium, potassium, rubidium, and cæsium, in Series I, are a group of soft, waxy metals of high luster and low boiling points. They decompose water readily, forming caustic bases. A study of their properties shows

that a gradual transition in properties accompanies the increase in atomic weights.

A similar variation in properties in accordance with the increase in atomic weight in a vertical series is well brought out in the study of the elements of the halogen group. At the head of each vertical series are placed some general formulas for the oxides and hydroxides of the elements in the series beneath. R is the general symbol for an atom of the element under consideration. Thus in Series I the general formula of the oxide is R_2O, and we have the oxides Li_2O, Na_2O, K_2O, Cu_2O, and so on.

These general formulas may be extended to include other compounds, as the chloride, nitrate, and sulphate:

	Series I		Series II	
	Formula	Illustration	Formula	Illustration
Oxide	R_2O	K_2O	R_2O_2 $(=2\,RO)$	CaO
Hydroxide	ROH	KOH	$R(OH)_2$	$Mg(OH)_2$
Chloride	RCl	KCl	RCl_2	$HgCl_2$
Nitrate	RNO_3	KNO_3	$R(NO_3)_2$	$Zn(NO_3)_2$
Sulphate	R_2SO_4	K_2SO_4	RSO_4	$BaSO_4$

	Series III	
	Formula	Illustration
Oxide	R_2O_3	Al_2O_3
Hydroxide	$R(OH)_3$	$Al(OH)_3$
Chloride	RCl_3	$AlCl_3$
Nitrate	$R(NO_3)_3$	$Al(NO_3)_3$
Sulphate	$R_2(SO_4)_3$	$Al_2(SO_4)_3$

It can be seen from the study of these general formulas that there is a regular increase in valence as we proceed from the first series to the seventh.

496. Position of the Inert Gases and of Hydrogen. — With the discovery of argon and other inert gases, considerable discussion arose as to their proper place in the periodic system. Since no compounds of these elements are known, they cannot be properly placed in any one of the vertical series. Accordingly it has been deemed best to form a separate vertical series for these elements at the beginning of the classification, and mark it Series 0. Including these inert elements, the first two short periods have eight elements each, while the first long period has eighteen.

It will be noticed that hydrogen is not placed in the table given on page 452. Since it has the smallest atomic weight, its natural position would be the beginning of the classification. If, however, it were placed in Series 0, it would be classed with the inert elements from which it differs decidedly in its properties. A similar difficulty would arise if hydrogen was placed in Series I, which contains the alkali metals. The position of hydrogen is so uncertain that it is left out of many periodic tables.

497. Significance of Vacant Spaces in Table. — It will be noticed that the series of elements is almost complete until the atomic weight of 145 is reached, while among the elements of a greater atomic weight many vacancies exist. Considerable speculation has arisen as to the meaning of these gaps. Perhaps in time other elements will be discovered to fill these blanks.

498. Value of the Periodic System. — *Mendelejeff's system has been of great value in predicting the discovery of new elements.* In fact, in the years immediately following the announcement of the law, when its validity was so much questioned, the fulfillment of Mendelejeff's predictions as to the existence and properties of elements then unknown

gave striking evidence of the correctness of the new system of classification. The table following shows the predictions and their verification in the case of an element which Mendelejeff called *eka-aluminum*, and which is now known as gallium:

PROPERTIES	PREDICTED	DISCOVERED
Atomic weight	About 69	69.9
Melting point	Low	30.1°
Specific gravity	About 5.9	5.93
Action of air	None	Slightly oxidized at red heat
Action on water	Decomposes at red heat	Decomposes at high temperatures

The predictions by Mendelejeff and their subsequent verification were equally striking in the cases of eka-boron (scandium) and eka-silicon (germanium).

The second use of the classification is in the adjustment and revision of atomic weights. In the early days of the classification many of the elements were improperly placed. It was suggested that this might be due to incorrect values for the atomic weights. This led to more accurate determinations of the atomic weights. In many cases results were obtained which permitted the elements to be placed in the table according to their proper relationships. Chemical research has been greatly stimulated by these revisions of atomic weights.

The development of a systematic study of the elements has been the greatest service of the periodic law. A knowledge of relationships has simplified the determination of the physical and chemical properties not only of the elements but of their compounds. Although the system of Men-

delejeff is not perfect, and no exact numerical relations have been found, the periodic classification is of great aid to the student of descriptive chemistry.

SUMMARY

The **principle of the Mendelejeff classification** of the elements is that "a periodic repetition of properties is obtained if all the elements be arranged in the order of the atomic weights."

While the elements in the **horizontal series** show a gradual transition in properties, the most closely related **families** or groups are arranged alternately in the vertical series.

The **Periodic System** has been of great value in (*a*) predicting the discovery of new elements, (*b*) the adjustment and revision of atomic weights, (*c*) the development of a systematic study of the elements.

EXERCISES

1. Show that there is in the second short period a transition from a strongly metallic element to a pronounced acid element.

2. Show by illustrations that the Mendelejeff classification is a periodic one.

3. Using symbols, indicate two families of elements in each of the following vertical series — II, IV, VI.

4. Give formulas for the oxide, hydroxide, sulphate, nitrate, and chloride of indium (In).

5. Show that the placing of the inert elements as Series 0 does not alter the periodic nature of the table.

6. What two uses of the table were of great value in securing its acceptance by chemists?

7. How may a student use the table profitably in the study of chemistry?

CHAPTER XXXVIII

INDUSTRIAL CARBON COMPOUNDS

499. Organic Chemistry. — The term organic chemistry owes its origin to the notion that a force different from that governing the mineral kingdom was necessary for the formation of nearly all compounds produced by plants and animals. This belief was overthrown by Wöhler in 1828, but organic chemistry is still the name commonly applied to the study of the carbon compounds. Carbon unites with other elements to form a very large number of compounds, most of which have a complex structure. As a rule, carbon compounds are only slightly ionized by water.

FIG. 143. — OIL WELLS.

500. Sources. — Coal, wood, and petroleum are the sources of a multitude of useful carbon compounds. Cellulose, the chief constituent of the cell walls of plants, is extensively employed in making paper, guncotton, collodion, and celluloid. The fat of cattle, hogs, sheep, fish, and whales is used in the manufacture of a large number of substances. Useful oils and fats are obtained from the seeds of cotton, hemp, and flax ; from the fruit of the oil palms, the cocoanut palm, and the olive tree. In fact, a great variety of plants furnish valuable oils. Milk is the source of butter, cheese, casein, and milk sugar, all of which are of great industrial importance. Starch is obtained in this country chiefly from corn ; sugar from sugar cane, beets, and the sugar maple.

501. Destructive Distillation. — When soft coal is heated in the absence of air, volatile substances pass off, and coke is left as a residue. A similar change takes place when either wood or bone is heated without air. The process of decomposing complex organic substances by heat in closed vessels and condensing the vapor of the liquid products, is termed *destructive distillation*. On account of the valuable substances obtained by the destructive distillation of soft coal and wood, these operations are carried out on a large scale.

502. The Destructive Distillation of Soft Coal is an extensive industry for obtaining illuminating gas, coke, and valuable by-products, including coal tar and ammonia. From coal tar, a great variety of useful substances is made.

503. Illuminating Gas. — The manufacture of enriched water gas and of producer gas has been treated (§§ 335

and 336). The making of illuminating gas from soft coal begins with the destructive distillation of the coal. This is carried on in long retorts placed in either a horizontal, an inclined, or better, a vertical position, and heated by coke or by producer gas (Fig. 144). Connected with each retort is a pipe which conveys the hot gases from the retorts to a large pipe, called the *hydraulic main*, through which water flows. The gases coming from the retorts are discharged under the water, which

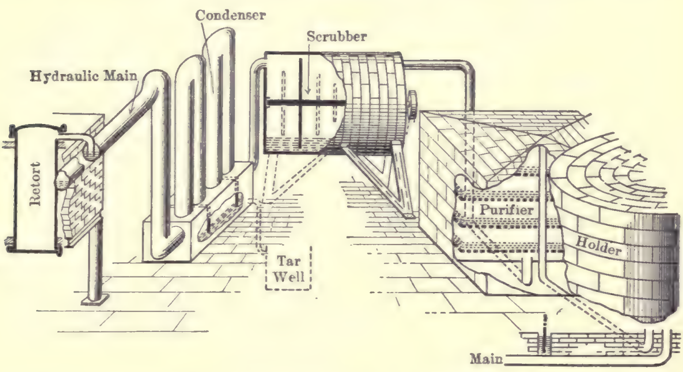


FIG. 144. — MANUFACTURE OF ILLUMINATING GAS.

serves as a seal to prevent the backward flow of gas, when a retort is opened and the pressure thereby decreased.

From the hydraulic main, the hot gases pass to a *condenser*, where cooling by air or water takes place and some of the tar is deposited. On leaving the primary condenser, the gas passes to a *tar extractor*, which removes the remainder of the tar by causing the gas containing tar vapor to impinge against sheets of metal. Next to the tar extractor is placed *an exhauster*, which is used to maintain the desired pressure in the retorts and to force the

gas through a series of scrubbers and purifiers into a gas holder. The tar extractor and exhauster are not shown in the figure.

The *scrubbers* are horizontal cylinders, each of which is divided by several vertical partitions. Through the center of each scrubber passes a horizontal shaft carrying a series of paddle wheels. As the paddle wheels revolve, the blades at one instant dip in the absorbing liquid of the purifier, and the next instant present a large wet surface to the gas passing through the apparatus. By the use of scrubbers, naphthalene, cyanogen, and ammonia are absorbed. Between the cyanogen scrubber and the ammonia washer is a secondary condenser, which is used to cool the gas so that any ammonia it contains will be absorbed by the water flowing through the ammonia scrubber. After the removal of ammonia, the gas is conducted through a series of *purifiers* to remove hydrogen sulphide. The purifiers contain layers of wood shavings coated with ferric oxide. The purified gas is measured by a large gas meter and stored in a *gas holder.*

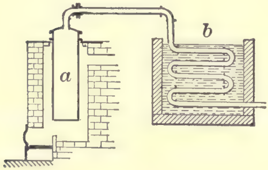


FIG. 145.

504. The Destructive Distillation of Wood is carried on in a retort (Fig. 145) connected with a condenser. The primary products of the distillation are gas, pyroligneous acid, wood tar, and charcoal. From the pyroligneous acid, several valuable compounds are obtained. Wood alcohol, acetic acid, and acetone are some of them.

505. Boneblack is the residue remaining after bones have been heated in a retort. The volatile matter produced during the process is sometimes collected and worked into

useful substanees. Before the heating in the retort takes place, grease is frequently removed from the bones by a suitable solvent, and gelatine is sometimes prepared by boiling them in water under pressure.

506. Fractional Distillation. — When a mixture of water and alcohol is distilled, the liquid commences to boil at a temperature near 78° C., the boiling point of alcohol. As the distillation continues, the boiling point rises until a temperature a little above that of boiling water is reached. While the distillation is going on, the distillate is generally separated into *fractions* by collecting the distillate in different vessels. One fraction of the distillate is collected during a definite rise in the temperature of the boiling liquid, a second portion of the distillate during another rise, and so on. The fraction first collected contains a large percentage of alcohol, while the fractions collected during the latter part of the process will be composed chiefly of water. By repeating the distillation of the fractions, the original mixture can be separated into two parts, one containing 95 per cent alcohol and the other nearly pure water.

Fractional distillation is the partial separation of two or more miscible liquids by distilling the mixture and collecting fractions of the distillate in different vessels.

507. Distillation of Petroleum. — Petroleum may be separated into useful substances by fractional distillation, but oil refiners generally combine fractional distillation with a kind of destructive distillation. As the distillation of the petroleum proceeds, the boiling point of the liquid in the still (Fig. 146, *A*) rises. When a portion of the vapor is condensed and made to drop into the hot oil in the still, it at once becomes superheated and its compounds decom-

pose into other compounds having a lower boiling point. A little carbon separates during the operation. The decomposition of the higher compounds of the oil is termed *cracking*.

The distillate from the crude oil is first separated into three fractions. This is accomplished by two air-cooled condensers, *B* and *C*, from which the successive fractions

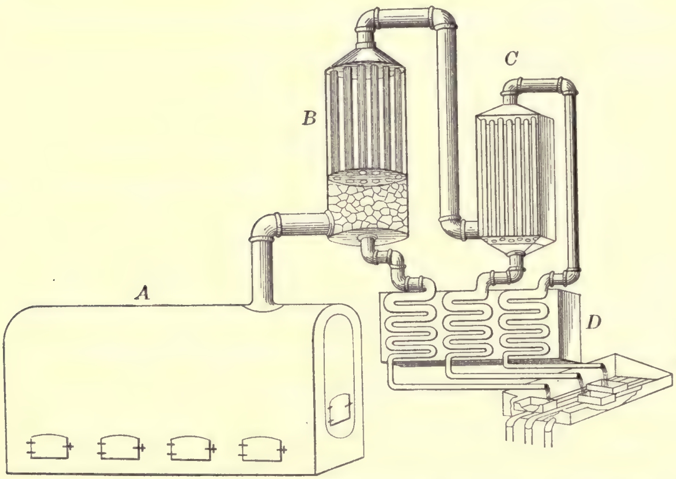


FIG. 146. — FRACTIONAL DISTILLATION OF CRUDE PETROLEUM.

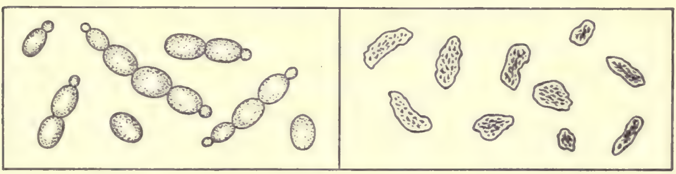
pass through three coils of pipe, immersed in a tank of water, *D*, in which the condensing process is completed. The fractions are run into different storage tanks by means of the distributing sink, *E*. Coke is left in the still. Each of the three fractions of the distillate is then redistilled, and treated so as to yield substances for which there is a demand. By varying the treatment of the petroleum during distillation, and by distilling under reduced pressure, the products obtained can be varied.

Gasoline, naphtha, benzine, kerosene, gas oils, lubricat-

Robert Kennedy Duncan (1868–1914) was born at Brantford, Ontario. From 1910 to 1914 he was director of the Department of Industrial Research of the University of Pittsburgh, and was the founder of the unique system of coöperation between science and industry in operation at the Mellon Institute of the University of Pittsburgh. He was a man who possessed great literary ability and who narrated the great discoveries of modern physical science in language easily understood by the layman, having a style as fascinating as that of a novelist. He was the author of "The New Knowledge," "The Chemistry of Commerce," and "Some Chemical Problems of To-day."

ing oils, vaseline, and paraffin are the more important substances obtained from crude petroleum. Paraffin is separated from a fraction of the petroleum distillate by artificial chilling.

508. Fermentation. — The term "yeast" is applied to cultures of yeast plants. There are several varieties of yeast; these plants are all microscopic in size (Fig. 147) and secrete powerful catalytic agents called *enzymes*. The most important enzyme, called *zymase*, has the power



a *b*

FIG. 147. — YEAST CELLS, HIGHLY MAGNIFIED.

a, living; *b*, dead.

of converting fermentable sugars into alcohol and carbon dioxide.

When yeast is placed in a warm, dilute solution of molasses, bubbles of a gas, carbon dioxide, soon cause the liquid to foam and alcohol is generated. *Fermentation* is a chemical change brought about by living organisms or by catalytic agents, called enzymes, secreted by them. Gases are frequently evolved during fermentations, so that the liquid becomes covered with froth. When preserves ferment, they are commonly said to "work." In the home, yeast is used to generate carbon dioxide in the dough of yeast bread. The bubbles of gas make the bread light and more digestible. The alcohol produced is driven off when the bread is being baked.

509. Production of Alcohol. — Ordinary alcohol is made in large quantities from grain or potatoes by the process of fermentation. Both of these substances contain a large quantity of starch. This is converted into maltose, $C_{12}H_{22}O_{11} \cdot H_2O$, by *diastase*, an enzyme contained in the malt (§ 510) that is added. The malted mixture is agitated with water at 63°C. The liquid is then cooled, diluted with water, and yeast added. The zymase formed by the yeast brings about the following reaction with the sugar, maltose :

$$C_{12}H_{22}O_{11} \cdot H_2O \longrightarrow 4\,C_2H_5OH + 4\,CO_2$$

When molasses (cane sugar) is used, the process is similar, except that no malt is necessary. The cane sugar is first converted into dextrose and levulose by a ferment known as *invertase*, also produced by the yeast plant.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}$$

Then the zymase from the yeast brings about the alcoholic fermentation of the two simple sugars :

$$\underset{\substack{\text{dextrose or}\\\text{levulose}}}{C_6H_{12}O_6} \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

The alcohol is separated from the resulting solution by repeated distillations.

510. Alcoholic Beverages. — Beer is the product obtained by the fermentation of malt. Barley is placed in a warm moist room until the kernels germinate. When the rootlet has grown to be two thirds the length of the kernel, the grain is heated to stop the growth. During the germination the starch in the barley is converted into maltose. The *malt* thus obtained is ground and boiled

with water. Yeast is added to ferment the malt sugar. The fermented liquor is filtered and water added to produce a beer or ale of the desired concentration. . Rice and glucose are often used to replace barley. Hops and other flavoring materials are also utilized. Beer contains from 3 to 5 per cent alcohol in addition to soluble materials from the grain.

Wines are produced by the fermentation of fruit juices which contain grape sugar (glucose). After fermenting, the liquor is allowed to settle and the clear liquid is drawn off. The wine thus produced, in addition to 7–15 per cent of alcohol, contains soluble materials derived from the fruit or produced in the fermentation. Whisky is made by distilling a beer obtained from rye or corn, so that the percentage of alcohol is increased to about 25–45 per cent. Brandy, resulting from the distillation of wine, may contain 50 per cent alcohol; and rum and gin, derived from fermenting molasses, possess about 30 and 40–80 per cent respectively. All of these distilled liquors contain minute quantities of flavoring materials and traces of acid.

511. Vinegar.—Dilute solutions of alcohol, such as are represented in weak wines, or hard cider, when exposed to the air, undergo a fermentation which results in the oxidation of alcohol to acetic acid. *Vinegar* is the liquid that results from this action; it is a dilute solution of acetic acid containing substances that give it color and modify its flavor. Vinegar is sometimes manufactured by what is called the *quick vinegar process.* Dilute alcohol, to which a certain amount of beer or malt extract has been added, is allowed to trickle over a mass of wood shavings that have been previously treated with vinegar in order to insure the presence of the fermenting or-

ganism. The porous mass of shavings makes possible free contact with air, which furnishes the necessary oxygen.

512. Soap Making. — No technical process depends more upon the skill of the operator than the manufacture of soap. In general, soaps may be classed as boiled, semi-boiled, or cold process. Boiled soaps are produced by boiling fats with sodium hydroxide and carbonate. They are often called settled or grain soaps because, during the process of manufacture, the glycerine is separated from the soap. Semi-boiled soaps contain all of the glycerine derived from the fats. Cold process soaps are formed by the direct combination of the fat and alkali, without the aid of external heat.

Most hard soaps used for household purposes are boiled soaps. Soap is made in large iron kettles, fitted with two sets of steam pipes; one, a closed coil to supply heat, and the other an open coil to deliver steam through the charge to keep it stirred. Melted fat and about one fourth the quantity of alkali required for complete saponification are run into the kettle and the steam turned on. The concentration of the alkali is regulated by the kind of fat used. When the mixture has become homogeneous, a more concentrated alkali is added and the boiling continued until a sample shows that the product has the desired consistency. Salt is then added, and the soap, being insoluble in brine, separates. The kettle is allowed to remain quiet for several hours and the soap collects on top of the liquid. This liquid is called *spent lye.* It contains glycerine, water, salt, and impurities from the alkali and fat. The spent lye is drained off, the salt and glycerine are separated from it, and the layer of soap is boiled with sufficient alkali to complete the saponification. During this boiling, rosin is sometimes added. Pure rosin soaps have strong

cleansing properties, but are too soft and sticky for general use.

The soap when taken from the kettle is often mixed with one or more of various fillers, such as sodium carbonate, borax, and sodium silicate. Coloring materials and perfumes may also be added. Soaps that float are made light by having air forced through them while they are in the pasty condition. If a good quality of soap is dissolved in alcohol and then dried, a transparent soap is obtained. Sugar and glycerine are often used in the manufacture of transparent soaps. Most soap powders consist essentially of hard soap, ground with sodium carbonate.

513. Starch. — Starch is found as granules in the cells of plants. These granules consist of a wall of starch cellulose within which is soluble starch. Starch is insoluble in cold water, but boiling water causes the walls of the starch granules to burst, and the soluble starch enters solution. Much starch is obtained from corn and potatoes.

PRODUCTS OBTAINED FROM CORN

Corn Kernel

- Germ
  - Corn Oil
    - Rubber Substitute
  - Oil Cake
    - Cattle Feed
- Endosperm
  - Starch
    - N. P. Corn Syrup
    - Export Corn Syrup
    - 70 Sugar
    - 80 Sugar
    - Anhydrous Sugar
    - Table Syrups
    - White Dextrine
    - Sp. White Dextrine
    - Canary Dextrine
    - Sp. Dark Canary
    - American Gum
    - British Gum
    - Pearl Starch
    - Powdered Starch
    - Laundry Starch
    - Thin Boiling Confectioners
    - Thin Boiling Laundry
    - Corn Starch
    - Ivory Starch
    - Grits
  - Gluten
    - Cattle Feed
- Hull
  - Cattle Feed

No matter what the source, the method of preparing starch is the same. The material is crushed, then macerated with water, and the milk-colored liquid filtered through cloth fine enough to prevent all besides the water and starch from passing. The starch is allowed to settle to the bottom of the containing vessel, from which it is afterwards removed and dried.

Fig. 148. — Bringing Sugar Cane to the Factory.

514. Sugar Manufacture and Refining. — Sugar is obtained from the juices of the sugar cane and beets. After extraction, slaked lime is added to the juice to prevent fermentation and to precipitate the albuminous substances coming from the plant cells. The solution is then filtered through cloth and evaporated in a vacuum pan at a temperature of about 66° C. If the evaporation were carried on under ordinary pressure, the temperature would become sufficiently high to convert the saccharose into a mixture of glucose and fructose.

As soon as a sample taken from the vacuum pan shows that sugar will crystallize when the syrup cools, the solution is removed from the pan and allowed to cool. The crystals are dried in centrifugal machines. The product obtained is usually raw sugar which must be refined before being placed on the market. Nearly all sugar refineries are in the northern states.

The raw sugar is dissolved in large vats and the syrup pumped to the top of high buildings, where it is mixed with lime and a little monocalcium phosphate to remove any albuminous material that may have been left in the sugar. The syrup is then filtered through long sacks, called bag filters, to remove the coarse impurities that are suspended in the solution. After this, the liquid is filtered through boneblack to remove the coloring matter. The purified syrup is boiled in vacuum pans as in the case of raw sugar.

Crystals of pure sugar have a pale, yellowish tint. As most people are ignorant of this fact and demand that a white sugar be sold them, the sugar refiners add some blue pigment to the sugar, for example ultramarine. The blue counteracts the yellow and causes the sugar to appear white.

SUMMARY

Organic chemistry is the chemistry of the carbon compounds.

Carbon compounds are derived chiefly from petroleum, coal, and plants.

Destructive distillation is the conversion of complex substances into simpler substances by means of heat in the absence of air. Volatile substances pass off and a solid residue is left.

Fractional distillation is the more or less complete separation of a mixture into its constituents by making use of the different

temperatures at which the ingredients boil and their vapors condense.

Alcohol is partially separated from water by fractional distillation.

Gas, wood alcohol, acetone, acetic acid, and charcoal are important substances resulting from the **destructive distillation of wood.**

Illuminating gas, ammonia, tar, and coke are some of the substances obtained by the **destructive distillation of soft coal**.

Gasoline, naphtha, benzine, kerosene, vaseline, and paraffin are **obtained from petroleum.**

Fermentation is a chemical change brought about by living organisms or by catalytic agents secreted by them.

An **enzyme** is a catalytic agent secreted by a living organism.

Several of the sugars are converted into alcohol, and alcohol is converted into acetic acid by processes of fermentation.

Soap is made by the reaction between sodium or potassium hydroxide, on the one side, and animal or vegetable oils and fats, on the other side.

Starch is formed in the cells of plants. It occurs in small granules, which are readily brought into suspension by stirring with water and thus separated from the plant tissues.

Sugar is generally obtained from the sap of the sugar cane or from the sugar beet. The sugar solutions are evaporated to crystallization in vacuum pans. The crude sugar is dissolved in water and the solution passed through a boneblack filter to remove the coloring matter.

EXERCISES

1. Name five organic substances used in the home and mention a natural source of each.

2. What is the meaning of destructive distillation?

3. Mention important substances resulting from the destructive distillation of soft coal. From distillation of wood.

4. Give the important steps in the manufacture of illuminating gas from soft coal.

5. What are four important products obtained during the manufacture of illuminating gas from soft coal?

6. What is fractional distillation?

7. Are gasoline and kerosene chemical compounds? Why do you think so?

8. How is paraffin obtained from petroleum?

9. What is the meaning of the term "fermentation"?

10. Name three important substances produced by fermentation.

11. How is alcohol made from potatoes?

12. What important chemical changes take place when sweet cider changes to vinegar?

13. How is soap made?

14. What are the principal constituents of soap powders?

15. Why is not boiling water used to prepare starch from corn?

16. Name three important substances obtained from corn.

17. What substance is used to remove the coloring matter from crude sugar?

18. Why are sugar solutions boiled in vacuum pans?

CHAPTER XXXIX

CLASSES OF CARBON COMPOUNDS

515. Structural Formulas. — Little advance was made in the study of carbon compounds until chemists began to represent the arrangement of the atoms in a molecule by structural formulas. A structural formula may be considered as a map of the molecule.

516. Reason for the Large Number of Carbon Compounds. — Atoms of nitrogen, to a limited extent, have the power of uniting with other atoms of nitrogen, forming nuclei, to which other elements attach themselves. A similar statement is true in the cases of several other elements. Carbon has this power to an almost unlimited extent. The ability of carbon atoms to unite with other carbon atoms to form stable nuclei, to which atoms of other elements join, accounts for the multitude of carbon compounds known to exist.

517. Hydrocarbons. — It is customary to commence the study of the carbon compounds with a consideration of compounds containing hydrogen and carbon only, that is, the *hydrocarbons.*

Methane or marsh gas is the hydrocarbon having the simplest structure. Its molecule contains one carbon atom in combination with four hydrogen atoms. In structural formulas, the valences of the elements considered are represented by dashes. The valence of carbon in nearly all of its compounds is four and the

valence of the hydrogen atom is one. $\begin{array}{c} | \\ -C- \\ | \end{array}$ represents the carbon atom and shows its valence. H— shows that the valence of the hydrogen atom is one. $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$ is the structural formula for methane and shows that four hydrogen atoms having a valence of one are united to one carbon atom having a valence of four. When two atoms of carbon are joined by a single valence bond, we obtain the nucleus $\begin{array}{cc} | & | \\ -C- & C- \\ | & | \end{array}$. The hydrogen compound containing this nucleus is $\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H-C-C-H \\ |\ \ \ | \\ H\ \ H \end{array}$, ethane. In a similar way, the chain of carbon atoms might be extended and formulas for several members of the series derived.

518. Paraffin Series. — The following table (p. 476) gives the names, formulas, and some of the physical constants of a few members of this series, which is called the *marsh gas series* from the name of its first member, or the *paraffin series*, because paraffin includes some of the higher members of the series.

The general formula for the marsh gas series is C_nH_{2n+2}, in which n stands for the number of carbon atoms in the molecule. Thus hexane contains 6 carbon atoms; and twice 6, plus 2, or 14 hydrogen atoms. It will be observed that the formula of each member differs from the preceding by CH_2; such a series is called a *homologous series*.

PARAFFIN SERIES

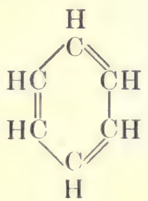
	FORMULA	MOLECULAR WEIGHT	BOILING POINT	FREEZING (OR MELTING) POINT	
Methane	CH_4	16	– 164°C	—	Ordinarily gaseous
Ethane	C_2H_6	30	– 89.5	—	
Propane	C_3H_8	44	– 38	—	
Butane	C_4H_{10}	58	+ 1	—	
Pentane	C_5H_{12}	72	36	—	Liquid
Hexane	C_6H_{14}	86	71	—	
Hexadecane	$C_{16}H_{34}$	226	288	18°	Solid
Octodecane	$C_{18}H_{38}$	254	317	28	

With increasing molecular weight, there will be noticed a rising of the boiling point and the tendency to assume the solid form in the higher members. It is mixtures of these compounds that occur in petroleum products.

There is only one methane, one ethane, and one propane, but as soon as we reach butane it is possible to group the atoms in more than one way. This results in giving two butanes, $CH_3—CH_2—CH_2—CH_3$, normal butane, and $\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\!\!>\!CH$, isobutane, both of which are known. There are 4267 pentadecanes, $C_{15}H_{32}$, theoretically possible.

519. Olefine Series.—When two adjacent carbon atoms are joined by a double bond, a new series of hydrocarbons, the *olefine* or ethylene series, results. The members of this series have the general formula C_nH_{2n}. Olefiant gas, a valuable constituent of illuminating gas, is the simplest member of the series. Its structural formula is $\begin{matrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{matrix}$.

520. Other Series. — If two adjacent carbon atoms are joined by a triple bond, the *acetylene series* results. The general formula for members of this series is C_nH_{2n-2}. Acetylene, H—C≡C—H, is the first member of the series. In addition to the hydrocarbons already mentioned, many other series exist. Some of these are called ring hydrocarbons because their structural formulas show a ring formation. Many of them have aromatic odors and give the series the name *aromatic*. Benzene, derived from coal tar, has the structural formula:



This is the starting point of the aromatic series.

521. Methane, or Marsh Gas. — Methane, CH_4, is a colorless, odorless gas which, when pure, burns with a nonluminous flame. It is often formed during the decomposition of organic matter, as in swamps, hence its common name, *marsh gas*. It is the principal constituent of natural gas. In soft coal mines, the miners call it *fire damp*, as its mixture with air is a serious source of danger.

522. Acetylene. — Acetylene has been mentioned as resulting from the reaction of calcium carbide and water:

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

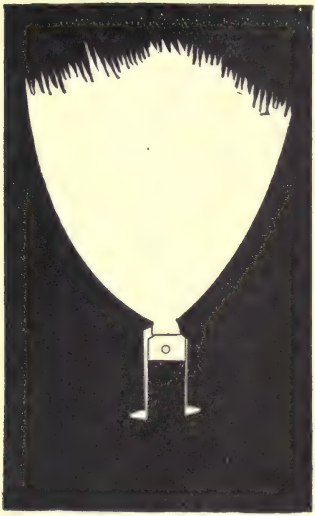


Fig. 149. — Acetylene Flame.

Ordinarily it burns with a smoky flame, but with a suitable burner it furnishes a brilliant light which nearly approaches daylight in color value (Fig. 149).

523. Benzene. — Benzene, or benzol, C_6H_6, is a light, colorless, volatile liquid, having a peculiar odor. Most of the benzol is obtained from the flue-gases of coke ovens, and from coal gas during its purification for illuminating purposes. It is also obtained from that portion of coal tar oil that boils at 80°–85°. Benzene burns with a smoky flame. It is a good solvent for resins and fats. Its principal use, however, is for the production of more complex compounds. Unlike the paraffin hydrocarbons, the coal hydrocarbons react with comparative ease, as with nitric and sulphuric acid, forming important compounds used in the preparation of dyestuffs.

524. Substitution Products are derived from hydrocarbons by the exchange of one or more hydrogen atoms for a corresponding number of atoms or radicals. The chlorine substitution products of methane are:

CH_3Cl, *monochlor*methane.
CH_2Cl_2, *dichlor*methane.
$CHCl_3$, *trichlor*methane (chloroform).
CCl_4, *tetrachlor*methane (carbon tetrachloride).

525. Methyl Chloride is a gas that can be easily compressed to a liquid, and is sold in the liquid state in metallic cylinders. It is used as a local anæsthetic, producing insensibility by freezing. It has also been used in ice machines.

526. Chloroform. — Trichlormethane, *chloroform*, $CHCl_3$, is a heavy, colorless, easily flowing liquid. It has a peculiar odor and a sweet taste. It is scarcely soluble in water. Chloroform is a most valuable anæsthetic and an important solvent. It is prepared by distilling alcohol or acetone with a solution of bleaching powder.

527. Carbon Tetrachloride, CCl_4, is prepared in the presence of antimony pentasulphide by passing through a heated earthenware tube the vapor of carbon disulphide mixed with dry chlorine. It is a low boiling, non-inflammable liquid. It is used as a solvent for grease and in certain types of fire extinguishers. It is a constituent of "Carbona."

528. Tri-iodomethane, *iodoform*, CHI_3, is a light yellow powder with a characteristic odor. It is useful as an antiseptic. Iodoform may be prepared by the reaction of iodine and alcohol rendered slightly alkaline.

529. Alcohols. — When one or more of the hydrogen atoms of a hydrocarbon are substituted by a corresponding number of hydroxyl (OH) groups, an alcohol is formed. It is a general rule that two hydroxyl groups cannot remain attached to the same carbon atom. An alcohol may be also looked upon as the first step in the oxidation of a hydrocarbon. Oxygen enters the molecule between an atom of hydrogen and a carbon atom. The alcohol of methane, CH_4, is methyl alcohol, CH_3OH. The alcohol of ethane, C_2H_6, is ethyl alcohol, C_2H_5OH.

Phenol or carbolic acid, C_6H_5OH, is an alcohol of benzene, C_6H_6. Glycerine or glycerol, $C_3H_5(OH)_3$, is an alcohol of propane, C_3H_8. In this case each carbon atom has a hydroxyl group attached to it.

530. Methyl Alcohol. — The source of methyl alcohol is the destructive distillation of wood. Impure methyl alcohol is sold as wood alcohol. It is a colorless liquid of low boiling point. It is used to a large extent as a solvent in the manufacture of varnishes. Wood alcohol is a very convenient fuel where small quantities of heat are required, because it burns with a clean flame of high heat value.

531. Ethyl or Grain Alcohol. — This is ordinary alcohol. The only important source of ethyl alcohol is the fermentation of certain sugars by yeast. Alcohol is obtained from the fermented liquid by fractional distillation. Glucose, $C_6H_{12}O_6$, a cheap sugar made from starch, is converted into alcohol and carbon dioxide by a ferment secreted by the yeast plant:

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

Ethyl alcohol resembles methyl alcohol in its properties. It is a low-boiling liquid, an excellent solvent for organic compounds, and it burns with a clean flame of high heat value. As a constituent of alcoholic beverages it is manufactured in enormous quantities. These beverages owe their intoxicating properties to the presence of alcohol.

532. Denatured Alcohol. — Denatured alcohol is ethyl alcohol to which wood alcohol or other poisonous substances have been added in order to make its use impossible in beverages and medicines. In countries where a

tax is imposed on alcoholic liquors, denatured alcohol is often exempt, so that the cost of the article in manufacturing operations shall not be prohibitive. Such an exemption law is in force in this country.

In the United States, methyl alcohol and benzene are two of the denaturing agents authorized by the Commissioner of Internal Revenue. The proportions by volume are as follows:

100 parts ethyl alcohol (not less than 90% strength)
10 parts methyl (wood) alcohol
$\frac{1}{2}$ part benzene

Such alcohol is classed as completely denatured, but there are many formulas for denaturization to suit special purposes.

353. Aldehydes and Ketones. — Three classes of alcohols, primary, secondary, and tertiary, are recognized by chemists. Primary alcohols have their hydroxyl group attached to a carbon atom bearing 2 hydrogen atoms. They contain the group

$$\begin{array}{l} H \\ | \\ -C-OH. \\ | \\ H \end{array}$$

Secondary alcohols have the general formula

$$\begin{array}{l} H \\ | \\ R-C-OH \\ | \\ R \end{array}$$

in which R may stand for various organic radicals. Their hydroxyl group is attached to a carbon atom combined with only one hydrogen atom. The tertiary alcohols have their hydroxyl group attached to a carbon atom combined with these organic radicals but with no hydrogen.

Aldehydes result from the oxidation of primary alcohols. It is supposed that a second oxygen atom enters the molecule between the carbon atom carrying the hydroxyl group and one of the hydrogen atoms. This causes two hydroxyl groups to become attached to the same carbon atom, producing an unstable compound, according to the rule stated in § 529. A molecule of water separates from the unstable compound leaving the group $-\underset{\substack{|\\ H}}{C}=O$ which is the distinguishing characteristic of an aldehyde. If we again use R to represent an organic radical, the changes may be represented as follows:

$$\underset{\text{alcohol}}{R-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}-OH} + O \longrightarrow \underset{\text{unstable compound}}{R-\overset{\substack{OH\\ |}}{\underset{\substack{|\\ H}}{C}}-OH} \longrightarrow H_2O + \underset{\text{aldehyde}}{R-\underset{\substack{|\\ H}}{C}=O}$$

During the process the alcohol loses two atoms of hydrogen and this gave the product the name aldehyde, that is, dehydrogenated alcohol.

Similar changes take place on the oxidation of secondary alcohols, and bodies called *ketones* result. A ketone is a compound corresponding to the general formula $R-\underset{\substack{|\\ R}}{C}=O$.

534. Formaldehyde is prepared by the slow oxidation of methyl alcohol. It has the formula $H-\underset{\substack{|\\ H}}{C}=O$. Formaldehyde is a very valuable disinfectant and preservative.

It is a gas at ordinary temperatures, but it comes into the market as a water solution known as *formalin.*

535. Acetone, $\begin{array}{l} CH_3 \\ | \\ C{=}O, \\ | \\ CH_3 \end{array}$ is a ketone derived from the products obtained by the destructive distillation of wood. Acetone is a colorless liquid possessing a characteristic odor. It is extensively used as a solvent for resins and gums, and in the manufacture of chloroform. It is an excellent solvent for acetylene. Prest-O-Lite cylinders are filled with asbestos that has been soaked in acetone. Acetylene under pressure is then dissolved in the acetone. When the pressure is removed by opening the valve of the tank, the acetylene passes out of solution and escapes.

ACIDS

When aldehydes are oxidized, acids result.

$$R{-}\underset{\displaystyle H}{\underset{|}{C}}{=}O + O \longrightarrow R{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}O$$

The group $-\underset{\displaystyle OH}{\underset{|}{C}}{=}O$, called the *carboxyl* group, is characteristic of organic acids. The hydrogen of the carboxyl group is the hydrogen of the acid that can be replaced by a metal. A number of organic acids are common useful substances.

536. Acetic Acid, $CH_3{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}O$ or $H(C_2H_3O_2)$, is the acid contained in vinegar. It is obtained from the destructive distillation of wood, and is produced by the

action of the acetic acid ferment (mother of vinegar) on impure dilute solutions of alcohol. The sugar of apple cider is changed to carbon dioxide and alcohol by a ferment of the yeast plant:

$$C_6H_{12}O_6 \longrightarrow 2\,CO_2 + 2\,C_2H_5OH$$

Then the acetic acid ferment converts the alcohol into vinegar:

$$C_2H_5OH + O_2 \longrightarrow H_2O + H(C_2H_3O_2)$$

Glacial acetic acid contains less than 1% of water; commercial acetic acid contains about 30% of the anhydrous acid. Acetic acid is used in the manufacture of white lead, as a solvent for various organic substances, and in the manufacture of the coal tar colors.

537. Oxalic Acid, $\begin{array}{l}COOH\\ |\\ COOH\end{array}$ or $H_2C_2O_4$, is obtained by heating sawdust in the presence of caustic soda, neutralizing a water solution of the product with calcium hydroxide, and then decomposing the calcium oxalate with sulphuric acid. Commercial oxalic acid contains water of crystallization as shown by the formula $H_2C_2O_4 \cdot 2\,H_2O$. Sublimed oxalic acid is anhydrous. Oxalic acid is a mild reducing agent and, on this account, is frequently used in the removal of iron rust and ink spots from white cloth, and for bleaching straw hats. It is also used for cleaning copper and brass. Oxalic acid is an important reagent in analytical laboratories and is used in calico printing, dyeing, and tanning.

The fact that oxalic acid is a poison should not be forgotten when the acid is kept in the house.

538. Important Fruit Acids. — *Tartaric Acid*, $H_2(C_4H_4O_6)$, is made from crude cream of tartar which deposits on the

side walls of wine vats during the fermentation of grape juice. Potassium acid tartrate, $KH(C_4H_4O_6)$, is *cream of tartar*.

Citric Acid, $H_3(C_6H_5O_7)$, is found in the juices of lemons, oranges, limes, gooseberries, and several other kinds of fruit.

ESTERS, OR ETHEREAL SALTS

539. Formation and Uses. — An ester and water are formed by the action of an acid with an alcohol. The reaction is analogous to that which takes place during the formation of a salt by neutralization. The alcohol may therefore be considered as taking the part of a base:

$$NaOH + H(C_2H_3O_2) \longrightarrow H_2O + \underset{\text{sodium acetate}}{Na(C_2H_3O_2)}$$

$$C_2H_5OH + H(C_2H_3O_2) \longrightarrow H_2O + \underset{\text{ethyl acetate}}{C_2H_5(C_2H_3O_2)}$$

The esters form an important group of compounds. Some are employed in medicine, while others are used in the preparation of perfumery. Many are used in making artificial fruit flavors. The characteristic flavor of the pineapple is due chiefly to ethyl butyrate; oil of wintergreen is methyl salicylate.

540. Nitroglycerin. — Nitroglycerin, $C_3H_5(NO_3)_3$, is an ester of an alcohol (glycerin) and nitric acid. It is prepared by the action of glycerin, $C_3H_5(OH)_3$, with a mixture of concentrated nitric and sulphuric acids:

$$C_3H_5(OH)_3 + 3\,HNO_3 \longrightarrow 3\,H_2O + C_3H_5(NO_3)_3$$

The sulphuric acid aids the action by uniting with the water formed during the reaction. The concentration of the free nitric acid is thus kept at maximum. Nitro-

glycerin is a highly explosive liquid at ordinary temperatures. *Dynamite* is nitroglycerin which has been absorbed by infusorial earth, or by a mixture of wood pulp and sodium nitrate.

541. Oils, Fats, and Soaps. — Oils and fats are esters of glycerine and various fatty acids. The chief constituent of beef tallow is glyceryl stearate, an ester of glycerine and stearic acid, commonly called *stearin.* It is formed by the reaction between one molecule of glycerine and three molecules of stearic acid.

When such a fat is boiled with a solution of sodium hydroxide, a molecule of glycerine and three molecules of sodium stearate, a hard soap, results from the reaction:

$$\underset{\text{glyceryl stearate}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{sodium hydroxide}}{3\,NaOH} \longrightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{sodium stearate}}{3\,NaC_{18}H_{35}O_2}$$

Common *hard soap* is a mixture of sodium salts of fatty acids, chiefly stearic, palmitic, and oleic acids. *Soft soap* is generally a mixture of the potassium salts of the fatty acids. The term *soap* is applied in general to any metallic salt of a fatty acid.

Sodium and potassium soaps are soluble in water. Soaps of the other common metals are insoluble.

542. Hard Water and Soap. — When a soluble soap, for example sodium stearate, is used with a water containing calcium ions, an insoluble calcium soap, calcium stearate, is formed:

$$2\,Na(C_{18}H_{35}O_2) + CaSO_4 \longrightarrow Ca(C_{18}H_{35}O_2)_2 + Na_2SO_4$$

The soap is said to be destroyed, as good suds cannot be formed until the calcium ions are removed from solution. This explains why hard water is not desirable

for washing purposes. The hardness of water is measured by its soap-destroying power. This is commonly due to the presence of calcium and magnesium ions in the water. Soap does not form suds with salt water because it does not go into solution. Salt water contains a large number of sodium ions and these keep the soap from dissolving.

543. Ether. — Ordinary ether, $C_4H_{10}O$, may be regarded as ethyl oxide, $(C_2H_5)_2O$. It is prepared by treating alcohol with a dehydrating agent, such as sulphuric acid:

$$2\,C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$$

Ether is a volatile, inflammable liquid, boiling at 35°C. It is used as a solvent and as an anæsthetic.

CARBOHYDRATES

The carbohydrates are chemical compounds composed of carbon united to hydrogen and oxygen, the last two elements being in the same proportion as in water. Starch, cellulose, glucose, and sugar are common carbohydrates.

544. Starch, $(C_6H_{10}O_5)_n$, is formed in the leaves of plants by the action of chlorophyll and sunlight on carbon dioxide and water:

$$6\,CO_2 + 5\,H_2O \longrightarrow C_6H_{10}O_5 + 6\,O_2$$

From the leaves, it is carried to other parts of the plant and is often stored in roots, tubers, and seeds. Starch reacts with dilute solutions of iodine. The product has a beautiful blue color. This reaction is used as a test for either iodine or starch.

Dilute acids convert starch into glucose, and much starch is used for this purpose. *Dextrin* is prepared by

heating dry starch to about 250° C. It is a valuable constituent of food, and is the adhesive used on the back of postage stamps.

Sprouting barley contains an enzyme (ferment) known as *diastase*, which is capable of converting starch into a sugar named *maltose*. In the manufacture of *malt*, the grain is allowed to germinate to produce the enzyme, after which the process is stopped by heating the barley to 60°. At a temperature of about 70° C., the diastase rapidly converts the starch which the grain contains into maltose and dextrose.

545. Cellulose. — The cell walls of plants are composed of cellulose, a compound having a percentage composition corresponding to the formula $C_6H_{10}O_5$. Absorbent cotton and the better grades of filter paper are pure cellulose. It is the chief constituent of straw and wood.

When boiled with acids, cellulose is slowly converted into a sugar called *glucose*. Cellulose dissolves without change in an ammoniacal solution of cupric hydroxide, known as Schweitzer's reagent. The cellulose can be precipitated from such a solution by the addition of alcohol. Concentrated solutions of sodium hydroxide convert cellulose into soda cellulose. This, when treated with carbon disulphide, yields viscose, a substance readily soluble in water. Cuprammonium solutions of cellulose and also viscose are used in the manufacture of artificial silks, which, since the finished product consists of cellulose, are more properly called luster celluloses. Cellulose is dissolved in zinc chloride in making the filaments for incandescent electric light bulbs. Acetic anhydride is used to convert cellulose into cellulose acetate, a substance useful in the manufacture of electric insulators and moving picture films.

546. Nitrocelluloses. — If the formula for cellulose is considered to be $(C_6H_{10}O_5)_2$, from two to six nitro (NO_2) groups can be introduced into the molecule. Thus, when pure cotton fiber is treated with a mixture of nitric and sulphuric acids, products are obtained which may contain two, three, four, five, or six nitro groups; the number depends upon the concentration of the acids and the time during which they are allowed to act.

The di-, tri-, tetra-, and penta-nitrocelluloses are known as *soluble guncotton*. Hexanitrocellulose is insoluble guncotton. *Collodion* is a solution of soluble guncotton in a mixture of alcohol and ether. Such a solution is used as liquid court plaster. *Celluloid* is made by dissolving the lower nitrates of cellulose in camphor and then, by heat and pressure, working the mass into the desired shape. *Explosive gelatine* consists of guncotton dissolved in nitroglycerin.

547. Sugars. — A very large number of sugars are known. *Fructose*, or fruit sugar; *glucose*, or grape sugar; and *saccharose*, or cane sugar, — are among the more important. Fructose and glucose have the empirical formula $C_6H_{12}O_6$; the formula for saccharose is $C_{12}H_{22}O_{11}$.

Glucose is converted by a ferment (zymase) secreted by the yeast plant into alcohol and carbon dioxide:

$$C_6H_{12}O_6 + \text{zymase} \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

This fermentation is made use of in the raising of bread and in the preparation of alcohol. It also is the cause of the formation of hard cider.

The manufacture of glucose from starch has already been referred to. Large quantities of glucose are used in making candies and table syrups. Common sugar, saccharose, is obtained from the sap of the sugar cane, sugar beet,

and sorghum. It is also the principal constituent of maple sugar (Fig. 150).

FIG. 150. — COLLECTING SAP FOR MAPLE SUGAR.

Saccharose is converted into glucose and fructose by boiling:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose and fructose have the same empirical formula.

Dilute acids hasten this action, which is known as inversion. For this reason vinegar is often added to sugar during the making of candy that is to be pulled.

Zymase does not convert saccharose into alcohol and carbon dioxide. However, the yeast plant secretes another ferment called *invertase* which changes saccharose

to a mixture of glucose and fructose. These, as has already been mentioned, can be fermented by zymase.

Common sugar melts at 160° C. to a colorless liquid which solidifies on sudden cooling to a transparent amber-colored mass, called *barley sugar*. When sugar is heated to 215°C., some water is expelled and a brown mass, *caramel*, is obtained.

SUMMARY

A structural formula is used to represent the arrangement of the atoms composing a molecule. On account of the large number of carbon compounds that have the same empirical formula, it is generally desirable to use a structural formula to represent graphically the chemical nature of a carbon compound.

A hydrocarbon is a compound composed of hydrogen and carbon only. The hydrocarbons of the **methane series** have the general formula C_nH_{2n+2}; those of the **olefiant series**, C_nH_{2n}; those of the **acetylene series**, C_nH_{2n-2}; and those of the **benzol series**, C_nH_{2n-6}. In these formulas n stands for the number of carbon atoms. Marsh gas, acetylene, and benzol are important hydrocarbons.

Substitution products are formed when one or more of the hydrogen atoms of a hydrocarbon are exchanged for an equivalent number of atoms of some other element, generally a halogen, or an equivalent number of radicals. Chloroform, iodoform, and carbon tetrachloride are common substitution products.

Alcohols may be considered as derived from hydrocarbons by substituting one or more hydroxyl groups for a corresponding number of hydrogen atoms. As a rule, two hydroxyl groups cannot remain attached to the same carbon atom. Methyl alcohol, ethyl alcohol, and glycerine are important alcohols.

Denatured alcohol is ethyl alcohol to which substances, generally methyl alcohol and benzene, have been added to make it unfit for use in beverages and in medicines.

Aldehydes contain the group $-\underset{\displaystyle H}{\overset{|}{C}}=O$. Formaldehyde is the most common aldehyde.

Ketones have the general formula $R-\underset{\displaystyle R}{\overset{|}{C}}=O$, in which R stands for an organic radical. Acetone is an important ketone.

Organic acids contain the carboxyl group $-\underset{\displaystyle OH}{\overset{|}{C}}=O$. Acetic acid, oxalic acid, and tartaric acid are familiar organic acids.

Esters or ethereal salts and water result from the reaction between acids and alcohols, the alcohol playing the part of a base. Sulphuric acid is generally used to aid the reaction. Nitroglycerin and animal and vegetable fats are esters.

A soap is a metallic salt of a fatty acid. Sodium and potassium soaps are soluble in water. Soaps of other common metals are insoluble.

A water is said to be hard when it contains some substance that will react with washing-soap to yield an insoluble soap.

Ether is ethyl oxide, $(C_2H_5)_2O$.

Carbohydrates are compounds containing carbon in combination with hydrogen and oxygen; they always contain two atoms of hydrogen for each atom of oxygen in the molecule. Starch, cellulose, glucose, and sugar are common hydrocarbons.

EXERCISES

1. Why is it frequently desirable to use the structural formula of an organic compound?

2. What is a hydrocarbon?

3. A hydrocarbon of the methane series contains three carbon atoms. Give its structural formula.

4. How many pentanes (C_5H_{12}) are possible? Write their structural formulas.

5. What is the structural formula for acetylene?

6. Why is carbon tetrachloride preferable to gasoline for the removal of grease spots from clothing in the home?

7. Define alcoholic fermentation; acetic fermentation.

8. What is an alcohol?

9. Give the formulas for three common alcohols.

10. What is denatured alcohol? Why is alcohol denatured?

11. What group of elements is characteristic of aldehydes?

12. What relation does formaldehyde bear to wood alcohol?

13. To what class of organic compounds does acetone belong?

14. What is Prest-O-Lite?

15. What group of elements is characteristic of organic acids?

16. What relation does acetic acid bear to alcohol?

17. To what class of compounds do animal and vegetable fats belong?

18. What is nitroglycerin? Dynamite?

19. What reaction takes place when soap is added to a water containing magnesium sulphate? Why?

20. Why do not soap suds form readily when soap is added to salt water?

21. Name three common carbohydrates.

22. How may alcohol be obtained from glucose? Equation.

23. Name a solvent for cellulose.

24. How is dextrin obtained from starch?

25. Would you expect to find dextrin in the crust or in the center of a loaf of bread?

26. Why is vinegar used in making sugar candy that is to be pulled?

27. What is barley sugar? Caramel?

CHAPTER XL

RADIUM AND RADIOACTIVITY

548. The Discovery of Radioactivity. — In 1896 the French chemist Becquerel, while investigating the penetrating powers of the rays emitted by phosporescent substances, happened to leave a compound of the element uranium spread out on the thick paper that inclosed a photographic plate. At the end of four weeks it was found that the plate had been affected by rays which had issued from the uranium compound, and which had penetrated the thick paper that inclosed the plate. Investigation showed that the result was in no way connected with the phosphorescent properties of the substance, since identical effects were observed whether the uranium compound was in the phosphorescent state or not. It appeared that the substance *continuously* gave off rays which produced photographic and electrical effects without being itself changed in the process.

This half-accidental discovery of Becquerel's led to investigations which have marked an important era in the history of chemistry. The term *radioactivity* was given to effects like those produced by uranium compounds.

549. The Discovery of Radium. — Madame Curie, a Polish woman resident in Paris, took up a series of researches along the line indicated by Becquerel's discovery. She found that all uranium compounds possess radioactivity, and hence that this is a property of the uranium *atom.*

Marie Slodowska Curie was born in Warsaw, Poland, in 1867. Her work began with the investigation of radio-activity first noticed by Becquerel in connection with uranium. She first isolated polonium, an element possessed of radio-activity in high degree, and later, in collaboration with her husband, Pierre Curie, made the epoch-making discovery of radium. For this work they received the Davy Medal of the British Royal Society, and shared with Becquerel, in 1903, the award of the Nobel Prize in Physics. Madame Curie succeeded her husband as the holder of one of the most important chairs of science in the world, the Professorship of Physics at the Sorbonne, University of Paris.

She then observed that pitchblende, the mineral from which uranium is usually obtained, is more radioactive than might be expected from the amount of uranium present. She reasoned that the mineral must, therefore, contain something more active than uranium. Working with this point in view, she found that bismuth and barium when extracted from pitchblende are radioactive. But ordinary bismuth and barium are not radioactive. Hence it was probable that when extracted from pitchblende the two metals contained small quantities of other elements, chemically similar themselves, and radioactive in a high degree. Madame Curie set out to find these elements.

She was soon able to show that bismuth obtained from pitchblende is in reality associated with an element many times more active than uranium. This element was named *polonium* in honor of her native country.

Her next work, done in collaboration with M. Curie, resulted in what probably always will be regarded as one of the greatest of chemical discoveries. This was the separation of a minute quantity of the element that is associated with pitchblende barium. It was named ***radium*** because of the extraordinary degree of radioactivity that it exhibited. The study of this remarkable substance has led to a better understanding of the nature of atoms, and to important changes in chemical theories.

550. The Nature of Radioactivity. — The peculiar characteristics possessed by radioactive bodies are due to emanations or radiations that they produce without undergoing any apparent change. Three types of such emissions have been recognized. They are designated by three Greek letters, α (alpha), β (beta), and γ (gamma). The first of these, the α emanation, has played the most important part in radium investigations. The basis of the

classification of the three types of rays was their penetrating power. The α type has the least power, though these rays will pass through a sheet of paper or even through very thin glass. The β rays have, roughly speaking, 100 times the penetrating power of the α type, and the γ rays have about 10,000 times the power of the α. These γ rays will traverse a foot of solid iron or six inches of the dense metal lead. They are identical with X-rays discovered by Roentgen. The β rays consist of minute particles of negative electricity (electrons).

The α radiation has been shown to be *atoms of the element helium* positively electrified. Helium has been recognized as an element for many years. It was first discovered by the aid of the spectroscope as a constituent of the gases that surround the sun. A few years before the radium investigations it was found as one of the rare gases of the atmosphere. Thus through radium we have found an actual case of the transmutation of elements, and, in a sense, the old, laughed-at idea of the alchemists has been revived in the mind of chemists.

Another extraordinary thing about radium is that it is continually giving off energy through its emanations. When a bit of radium is placed beside the bulb of a thermometer and the two are wrapped in a bit of cotton or wool, the thermometer stands a degree or two higher than the temperature of the room. But so far as ordinary observation reveals, the substance is absolutely unchanged either in properties or weight. Here we have an apparent contradiction of the law of the conservation of energy. Another and more striking experiment showing the continuous emission of energy is found in the *radium clock* (Fig. 151). A small quantity of radium bromide is contained in a metal tube from which are suspended two pieces of gold leaf. The leaves separate owing to the fact that

they are electrically charged by the effect of the radium. On diverging, the leaves touch the strips of metal on the inside of the bottle which contains the apparatus and discharge their electricity. They then fall together, are again charged by the radium, and again separate. Since the radium compound does not apparently diminish in producing this action, the clock will seemingly go on forever. In other words, we have realized a sort of perpetual motion.

These three examples will serve to show how radium seemed to upset established physical and chemical ideas. It remains for us to show how these things were reconciled with the older knowledge.

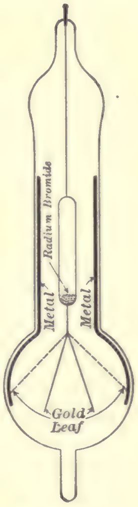


FIG. 151. — RADIUM CLOCK.

551. Radioactive Decay. — Let us consider further experimental facts. Radium is always found in ores that contain uranium, in the definite proportion of 1 part of radium for about 3,200,000 parts of uranium. Radium compounds when recrystallized from water solution are found to be inactive, but regain their activity on standing a few days. The water which was used in the process gives off a minute quantity of a gas, that, mixed with air, can be aspirated from one vessel to another, and that rapidly loses its activity, so that in a little over five days it is only half as active as before. Objects that come in contact with this gas, or that have been near radium, become active; but if these objects are rubbed with sandpaper, the activity is found to be attached to the scraping material; this acquired activity, however, decays to half its value in about thirty minutes.

These facts have been studied and satisfactory and consistent explanations have been found for the whole range of observations. This has been done by the aid of instruments so sensitive that quantities of radioactive materials can now be recognized that would be a million times too small to be detected by the older methods.

552. Radioactive Series. — In adopting these new explanations it was found necessary to abandon the old idea that an atom is an unchangeable thing. It is now believed that radioactive elements are continuously undergoing processes of decomposition. During the changes, two important things occur: (*a*) relatively *enormous amounts of energy* are liberated, and (*b*) new elements are produced. It appears that certain of the atoms explode from time to time, producing the various radioactive effects. Helium atoms result in many cases, and sometimes β and γ radiations. In each case, the greater part of the exploding atom remains intact and forms the atom of a new element. This explodes in its turn, and thus we have a series of radioactive elements resulting from one parent element. During the transformations, the atomic weights continually decrease. A helium atom weighs 4, and when one of these is evolved, we find that the atom which is left weighs 4 less than its parent atom.

Two main series of such radioactive transformation have been recognized. Uranium is the parent element in one series, and thorium in the other.

553. The Uranium Series. — Different radioactive elements vary greatly in the speeds with which they decompose. The less active ones decompose slowly, the more active rapidly. Thus, in the case of uranium, which is very slightly active, it has been calculated that it would

take 8,000,000,000 years for half of the atoms in a given mass to change into other substances. It would take another 8,000,000,000 years for half of the remainder to decompose, and so on. The "life" or period of one of these elements is measured by the time it would take for half of its atoms to change.

The uranium atom, atomic weight 238, in decomposing, produces an atom of helium, atomic weight 4, and an atom of uranium II, atomic weight 234, period 2,000,000 years. The transformation goes on through two other elements, uranium X, period 35.5 days, and ionium, period 200,000 years, to radium, atomic weight 226. This element has played the most important part in radioactive investigations because its period, which is 2500 years, is long enough to permit study, and at the same time short enough to give to the element a high degree of radioactivity.

Radium atoms in their explosions give off helium atoms and a new element described above as the gas obtained from solutions of radium salts. This is an extremely active substance whose period is 5.6 days. Its atomic weight is 222, and it has been identified by Ramsay as niton. The decompositions continue from this element through several others of extremely short period, ending with polonium, with a period of 202 days, and an atomic weight of 210. Some of these short-lived elements constitute the deposit found on substances that have been near radium salts. This, by loss of a helium atom, becomes an element of atomic weight 206. This is the value for lead and it is believed that this element is the final result of the series of uranium decompositions.

554. The Thorium Series. — Thorium is a comparatively rare element whose oxide has become commercially important in recent years as the chief constituent of gas

mantles. It is a radioactive substance of long period, probably 25,000,000,000 years. As we would expect from this figure, it is not a very active substance. But there are always found associated with the natural deposit of the thorium mineral small quantities of its decomposition products, and some of these are more active than radium. They are separated with the by-products during the process of purification, and we have thus an important source of radioactive material.

Thorium itself slowly produces mesothorium I with loss of a helium atom. This element is interesting because it is chemically identical with radium, and can only be distinguished from radium by the difference in its period, that of mesothorium being 7.9 years. It is an intensely active substance, which makes a good substitute for radium in studying radioactivity. Some eight or nine other elements have been recognized in tracing the series of thorium decompositions.

555. The Value of the Radium Discoveries. — On the discovery of radium, investigations were at once started in the hope that its extraordinary radiations might act as a cure for cancer. Its value for this purpose is still in doubt. This constitutes, so far, the only direct, practical application of radium.

As sources of energy the radioactive substances are truly remarkable. A bit of radium in changing down to lead gives out 300,000 times as much energy as does an equal weight of coal in burning. It has been observed that if chemists ever succeeded in producing gold from the atomic decomposition of elements of higher atomic weight, the energy liberated might be comparable in value to that of the gold itself.

The principal value of radium has been in giving us a

better understanding of the nature of atoms. It is believed that all atoms consist of minute particles, called electrons, which are identical with the β emanations of radioactive bodies, and which consist of nothing more nor less than negative charges of electricity. The explosions of radioactive atoms are due to spontaneous rearrangements of the electrons within the atom. It is believed that the atoms of all elements might undergo radioactive transformation if we could find a method of causing them to take place; and that the transmutations of elements are within the range of final possibility. According to this point of view, there is an inexhaustible amount of energy stored up in atoms, and it is conceivable that some day this may be made available. It will be necessary to find a way of inducing the transformations to take place, just as it was necessary for some one to find how to build fires to make the energy of fuels available. It is possible that all atoms are actually undergoing decomposition continuously, but at such slow rate that we are not able to observe the process.

With the conception of electrons, chemists are adopting new ideas of many things, such as valence and the processes of oxidation and reduction. For example, a univalent, electropositive element may be regarded as made up of atoms, which have a great tendency to lose one electron (a particle of negative electricity) and thus by its loss to remain positively charged. A univalent, electronegative element has atoms which have a tendency to acquire an electron, and thus to become negatively charged. Divalent elements tend to lose, or to acquire, *two* electrons, and so on.

The young student is likely to wonder why so much importance is attached to a thing of theoretical interest like radium. It appears to him that a substance of which

there are only two or three grams in the world, and whose market value is something like $1,800,000 per ounce, cannot be of much real use. But in taking this point of view he forgets two things. The first is that, in the main, practical discoveries and inventions follow theoretical development. The second is that there is, in the human mind, a need for understanding the things that are about us, and that this need is a more permanent part of human nature than even the desire for material progress. It is this latter need that the radioactive discoveries have satisfied in such high degree.

SUMMARY

Radioactivity is a name given to an action by which certain elements give off continuously large amounts of energy without undergoing chemical action.

The energy is given off in the form of rays or radiation which produce electrical and other effects. Three types of these rays are recognized, known respectively as the **α, β, and γ radiations**. They all have the power to penetrate solid substances, that of the α variety being very slight, that of the β somewhat greater, and that of the γ very great.

Following the discovery of **polonium** and **radium** by Mme. Curie, it was shown that the cause of radioactivity is a **decomposition of the atoms** of the elements that produce the effect.

The **α radiation** consists of positively charged helium atoms. This fact constitutes a case of transmutation of elements.

Since a radioactive element gradually decomposes, it follows that such elements have a life period. This is usually stated as the "**half life**," meaning the time it would take for half of the atoms in a given quantity to decompose. This period is 2500 years for radium. That of some of the elements is only a few

seconds, that of others is millions of years. The shorter the period, the greater the degree of radioactivity.

Two series of radioactive elements have been recognized. **Uranium**, the "parent" element in one series, by successive losses of radiation (including frequently, but not always, the α type helium atoms) passes into elements of lower and lower atomic weight. Radium and polonium are included in this series. Lead is believed to be the end of this series of decompositions.

A thorium series has also been recognized.

The radium discoveries are regarded as important chiefly because they have brought about **changes in important chemical theories**. We now believe that atoms of all elements are composed of large numbers of small particles, called **electrons**. These are regarded as minute charges of negative electricity. The β radiation consists of these particles.

EXERCISES

• 1. Why was the isolation of radium from pitchblende regarded as a brilliant piece of chemical work?

2. In what respects does radium differ strikingly from ordinary elements? In what respects does it resemble them?

3. Is it true that we could produce perpetual motion by means of radium? Explain.

4. Distinguish between the α, β, and γ radiations emitted by radioactive elements.

5. Why were radium and mesothorium I of especial value for purposes of radioactive study?

6. What is meant by the period of a radioactive element?

7. What means would you use to test a mineral for the presence of radioactive elements?

8. What relation is there between the period of a radioactive element and its degree of activity?

9. Explain how radioactivity has given a new conception of the character of atoms in general.

10. What is meant by saying that enormous amounts of energy are liberated by radioaction?

11. What ancient idea of the alchemists has been revived by the radium discoveries?

12. Name a radioactive element of very short period; one of very long period.

13. For what reasons is the price of radium very great?

14. What new conception of valence has resulted from the electron theory of atoms?

15. Why is radium always found in ores that contain uranium?

16. Why can we never expect to find radium in more than a very small amount in any mineral?

APPENDIX

I. PHYSICAL CONSTANTS

OF THE IMPORTANT ELEMENTS

Element	Symbol	Atomic Weights		Valence	Specific Gravity		Melting Point	Boiling Point
		Approximate	Exact O = 16		Water = 1	Air = 1	° C.	° C.
Aluminum	Al	27	27.1	III	2.7		657	2200
Antimony	Sb	120	120.2	III V	6.6		630	1600
Argon	A	40	39.88	——		1.38	−188	−186
Arsenic	As	75	74.96	III V	5.7		. . .	<360 volatile
Barium	Ba	137	137.37	II	3.8		850	950
Bismuth	Bi	208	208.0	III V	9.7		269	1435
Boron	B	11	11.0	III	2.4		infusible	3500
Bromine	Br	80	79.92	I	3.1		−7.3	59
Cadmium	Cd	112	112.4	II	8.6		321	778
Calcium	Ca	40	40.09	II	1.8		about 805	. . .
Carbon	C	12	12.00	IV	amorphous 1.4–1.9		infusible	3500
Chlorine	Cl	35.5	35.46	I		2.49	−102	−33.6
Chromium	Cr	52	52.0	II III VI	6.9		1505	2200
Cobalt	Co	59	58.97	II	8.7		1490	. . .
Copper	Cu	63.6	63.57	I II	8.9		1083	2310
Fluorine	F	19	19.0	I		1.26	−223	−187
Gold	Au	197	197.2	I III	19.3		1062	2530
Helium	He	4	3.99	——		0.13	−270	−268.5
Hydrogen	H	1	1.008	I		0.07	−259	−252
Iodine	I	127	126.92	I	4.9		114	184
Iron	Fe	56	55.85	II III	7.8		1520	2450
Lead	Pb	207	207.1	II IV	11.3		327	1525

Element	Symbol	Atomic Weights		Valence	Specific Gravity		Melting Point	Boiling Point
		Approximate	Exact O = 16		Water = 1	Air = 1	° C.	° C.
Lithium	Li	**7**	6.94	I	0.59		186	<1400
Magnesium	Mg	**24**	24.32	II	1.7		650	1120
Manganese	Mn	**55**	54.93	II IV	7.4		1225	1900
Mercury	Hg	**200**	200.0	I II	13.6		−38.8	357 Hydrarg[cut off]
Nickel	Ni	**58.7**	58.68	II	8.7		1450	. . .
Nitrogen	N	**14**	14.01	III V		0.96	−213	−195
Oxygen	O	**16**	16.00	II		1.10	<−218	−182
					white		white	
Phosphorus	P	**31**	31.04	III V	1.8		44.1	290
Platinum	Pt	**195**	195.2	IV	21.1		1753	. . .
Potassium	K	**39**	39.10	~~I~~	0.87		62.5	757 Kali
Silicon	Si	**28**	28.4	IV	2.4		1420	3500
Silver	Ag	**108**	107.88	I	10.5		961	1955 Argent[cut off]
Sodium	Na	**23**	23.0	I	0.97		97.6	877 natri[cut off]
Strontium	Sr	**87**	87.63	II	2.5		900	. . .
							rhombic	
Sulphur	S	**32**	32.07	II IV VI	2.0		114.5	444.6
Tin	Sn	**119**	119.0	II IV	7.0–7.3		232	1525
Zinc	Zn	**65**	65.37	II	7.1		419	918

II. TABLE OF SOLUBILITIES

S = soluble in water. I = insoluble in water. P = slightly (partly) soluble in water. Ia = insoluble in water and dilute acids

	Aluminum	Ammonium	Antimony	Arsenious	Barium	Bismuth	Cadmium	Calcium	Cobalt	Copper	Ferrous (Fe^{++})	Ferric (Fe^{+++})	Lead	Magnesium	Manganese	Mercurous (Hg^{+})	Mercuric (Hg^{++})	Nickel	Potassium	Sodium	Silver	Zinc
I Acetate $C_2H_3O_2$	S	S	—	—	S	—	S	S	S	S	S	—	S	S	S	P	S	S	S	S	S	S
I Bromide . Br . .	S	S	P	S	S	P	S	S	S	S	S	S	P	S	S	I	S	S	S	S	Ia	S
II Carbonate CO_3 . .	—	S	—	—	I	I	I	I	I	I	I	—	I	I	I	I	I	I	S	S	I	I
I Chlorate . ClO_3 .	S	S	—	—	S	—	S	S	S	S	—	—	S	S	—	S	S	—	S	S	S	S
I Chloride . Cl . .	S	S	P	S	S	P	S	S	S	S	S	S	P	S	S	I	S	S	S	S	Ia	S
II Chromate CrO_4 .	—	S	—	—	I	I	—	I	I	I	—	—	Ia	S	—	P	P	—	S	S	I	—
I Hydroxide . OH . .	I	S	P	S	S	I	I	P	I	I	I	I	I	I	I	—	I	I	S	S	—	I
I Iodide . I . . .	S	S	P	P	P	I	S	S	S	—	S	—	I	S	S	I	I	S	S	S	Ia	S
I Nitrate . NO_3 . .	S	S	—	—	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
II Oxide . . O . . .	I	—	I	P	S	I	I	P	I	I	I	I	I	I	I	I	I	I	S	S	I	I
III Phosphate . PO_4 .	I	S	—	—	I	I	I	I	I	I	I	I	I	I	P	I	I	I	S	S	I	I
II Sulphate . . SO_4 .	S	S	—	—	Ia	S	S	P	S	S	S	S	Ia	S	S	P	S	S	S	S	P	S
II Sulphide . S . . .	—	S	Ia	Ia	S	Ia	Ia	P	I	Ia	P	—	Ia	S	I	Ia	Ia	I	S	S	Ia	I
II Sulphite . SO_3 . .	—	S	—	—	I	—	S	P	I	S	P	—	I	P	—	—	—	I	S	S	S	P

III. GENERAL RULES FOR SOLUBILITY

Certain generalizations can be made concerning compounds shown in the table on the opposite page. The exceptions to these generalizations are few and unimportant.

1. All *sodium, potassium*, and *ammonium* compounds are *soluble* in water.

2. All *nitrates, chlorates*, and *acetates* are *soluble* in water.

3. All *chlorides* are *soluble*, except those of silver, mercury (mercurous), and lead (lead slightly soluble).

4. All *sulphates* are *soluble*, except those of barium, lead, and calcium (calcium slightly soluble). The silver and the mercurous sulphates are only moderately soluble.

5. All *carbonates* are *insoluble*, except those of sodium, potassium, and ammonium.

6. All *oxides* and *hydroxides* are *insoluble*, except those of ammonium, sodium, potassium, and barium; calcium hydroxide is slightly soluble.

IV. VOLATILITY OF COMPOUNDS THAT MAY RESULT FROM DOUBLE DECOMPOSITIONS

1. Compounds volatile at ordinary temperatures:

$$HCl \quad HBr \quad HF \quad H_2S$$

2. Compounds decomposing at ordinary temperatures yielding volatile products:

$$H_2CO_3\ (H_2O + CO_2)$$
$$H_2SO_3\ (H_2O + SO_2)$$
$$NH_4OH\ (H_2O + NH_3)$$

3. Compounds volatile at varying temperatures below 338° (boiling-point of sulphuric acid):

	Boiling-point		Boiling-point
H_2O,	100°	HNO_3,	86°
HCl (aqueous solution),	110°	HNO_3 (aqueous solution),	120°
HBr (aqueous solution),	126°	$HC_2H_3O_2$,	118°

V. APPROXIMATE WEIGHT OF ONE LITER OF COMMON GASES UNDER STANDARD CONDITIONS

Acetylene,	1.17 grams	Hydrogen sulphide,	1.53 grams
Ammonia,	0.77 "	Marsh gas,	0.72 "
Carbon dioxide,	1.98 "	Nitrogen,	1.26 "
Carbon monoxide,	1.26 "	Nitric oxide,	1.35 "
Chlorine,	3.20 "	Nitrous oxide,	1.98 "
Hydrogen chloride,	1.64 "	Oxygen,	1.44 "
Hydrogen,	0.09 "	Sulphur dioxide,	2.88 "

VI. PRESSURE OF WATER VAPOR, OR AQUEOUS TENSION

(In millimeters of mercury)

Temperature	Pressure	Temperature	Pressure
0.0° C.	4.6 mm.	21.5° C.	19.1 mm.
5	6.5	22.	19.7
10	9.2	22.5	20.3
10.5	9.5	23.	20.9
11	9.8	23.5	21.5
11.5	10.1	24.	22.1
12	10.5	24.5	22.8
12.5	10.8	25.	23.5
13	11.2	25.5	24.2
13.5	11.5	26.	25.0
14	11.9	26.5	25.7
14.5	12.3	27.	26.5
15	12.7	27.5	27.3
15.5	13.1	28.	28.1
16	13.5	28.5	28.9
16.5	14.0	29.	29.8
17	14.4	29.5	30.7
17.5	14.9	30	31.6
18	15.4	40	54.9
18.5	15.9	50	92.1
19	16.4	60	149.2
19.5	16.9	70	233.8
20	17.4	80	355.4
20.5	17.9	90	526.0
21	18.5	100	760.0

$C_{12}H_{22}O_{11}$ Cane sugar, sugar, suc

$C_6H_{12}O_6$ Glucose

$C_6H_{10}O_5$ Starch

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